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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennyslvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

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Revised Rules Governing Preparation and Presentation of Papers at General Meetings of the Rubber Division of the American Chemical Society

1. FOUR copies of each paper are to be in the hands of the Secretary six weeks prior to the meeting.
2. The author is to send in an abstract of not over 200 words along with his manuscript.
3. The chairman is to appoint, in addition to the two formal reviewers who approve the paper for presentation and publication, two more reviewers who will be expected to lead the formal discussion at the meeting. It is possible that the two formal reviewers may be willing to lead the discussion.
4. The reviewers are to submit their comments in DUPLICATE without signatures, and that the Secretary send one anonomous copy of each to the author of the paper. The author may use these comments in rewriting his paper, but he may not expand it beyond its original scope. The final paper for publication must be in the hands of the Secretary before it is presented at the meeting.
5. The discussion of papers is to be reported as far as practicable and be published in concise form, but the discussion is not to be published until after it has been revised by the authors of the discussion.
6. The authors and the reviewers are to give the Secretary the number of minutes to be allotted on the program for the paper, and the author is to be notified of the time allotted to him.
7. A paper should usually consist of the following parts:
   (*a*) Synopsis
   (*b*) Brief introduction
   (*c*) Main body, including experimental work
   (*d*) Conclusions
   (*e*) Bibliography.
8. In the presentation at a meeting, the author should never read his complete paper. He should use a comprehensive abridgment, and carefully think over his method of presentation beforehand. Properly made slides or charts are most helpful, and when discussing them, the speaker should talk to the audience, not to the screen.

9. The original and two extra copies of the drawings or data from which slides are to be prepared shall accompany the paper, and that the author should observe the following in the make-up of slides:

(*a*) Too much should not be put on one slide

(*b*) All curves should be distinctly drawn

(*c*) Letters and figures should be large enough when on the screen to be legible from the rear of a 100-foot room.

(*d*) Slides should be numbered.

10. Charts, curves, and tables for publication should conform with the recommendation on these matters given in the article in *Industrial and Engineering Chemistry*, Vol. 19, p. 755 (June, 1927); and bibliographies should conform to the standard practice of the Society publications.

Authors are reminded of the fact that in the American Chemical Society publications the metric system of units must be used, and that the English system may be used in addition.

New Books and Other Publications

Plantation Sheet Rubber Manufacture. Planting Manual No. 3. Published by Rubber Research Institute of Malaya. Kuala Lumpur, F.M.S. February, 1932. 62 pp.

The manual has been prepared to give the latest information concerning improvements in rubber estate factory practice regarding the coagulation of latex, the handling of coagulum, and the machining, drying, and smoking of sheet rubber. Technic in relation to estate factory practices is discussed in detail. [From *The Rubber Age* of New York.]

Ninth Report of Native Rubber Cultivation. 4th Quarter, 1931. Prepared by the Bureau of Agricultural Economics of the Netherlands Indian Department of Agriculture, Industry and Commerce. 22 pp. 1932.

Latest official figures and data on the production from native areas in the Dutch East Indies. The report indicates a certain decline in native activities, due to prevailing low prices, but substantial areas have not yet reached the tapping age and other large areas have grown to bearing but have not been tapped, showing a large potential yield which might come from these native holdings, in the event of more favorable price conditions. [From *The Rubber Age* of New York.]

The Law of Patents for Chemists. By Joseph Rossman, Washington, D. C. The Inventors Publishing Co., 1932. Cloth, 304 pages, $5\frac{1}{2}$ by $8\frac{1}{4}$. Indexed.

Chemists and chemical engineers interested in invention will find in this book a comprehensive and authoritative discussion of chemical patents with full information on the procedures essential for securing and enforcing their patent rights. A glossary is given of words and phrases most commonly used in patent law followed by appendices illustrative of official classes and chemical patent applications, statistics, annotated bibliography, and index. [From *India Rubber World.*]

A Wonder Book of Rubber. Published by The B. F. Goodrich Company, Akron, O. 50 pp. 1932. For free distribution.

An interesting story of rubber and the manufacture and use of rubber products. The booklet is entertainingly written and is profusely illustrated. It incidentally embodies the romance of the growth of the Goodrich Company and the ramifications of its activities. [From *The Rubber Age* of New York.]

Plastics and Rubber Year Book, 1932. Casa Editrice Pollini, Milan, Italy. Cloth, 144 pages, $6\frac{1}{2} \times 9\frac{1}{4}$ inches. Indexed.

This year book, in Italian, with preface in English, French, Italian, and German, is the first directory of the Italian molded plastics and rubber industries. Its publication was initiated for the benefit of suppliers of raw materials, chemicals, and modern machinery desiring to reach these rapidly developing branches of Italian manufacturing industry.

The lists include suppliers of plastic materials, plastic machinery, manufacturers, and users of molded products. Similarly, the rubber section contains classified lists of dealers in materials and machinery for rubber goods manufacturers. The work concludes with a listing of producers and users of ebonite. Each list is preceded by appropriate text descriptive of the nature of the materials and processes.

This publication is to be followed shortly by a similar one by the same publishers devoted to the Italian paint and varnish industry. [From *India Rubber World.*]

Dunlop 60% Latex. Dunlop Rubber Co., Ltd., Ft. Dunlop, Birmingham, England.

This illustrated brochure of 36 pages has for its object the introduction of the processes that have been discovered for utilizing rubber latex as raw material for industrial purposes. The production of Dunlop 60% concentrated latex and its many applications are interestingly set forth. [From *India Rubber World.*]

The Electrometric Determination of the Hydrogen Ion Concentration in the Latex of *Hevea Braziliensis* and Its Applicability to Technical Problems. By N. H. Van Harpen. Varekamp & Co., Medan, Sumatra, D. E. I. Paper, 458 pages, 7 by $9^1/_4$ inches. Graphs. Tables. Index.

In this thesis the author sets forth his exhaustive research on the methods of determining the p_H of latex. The book comprises 5 chapters as follows: General Introduction; Technic of Measuring Hydrogen Ion Concentration in Latex; Coagulation Phenomena of *Hevea* Latex; Coalescence in the Flocculation Stage; and Applications of Hydrogen Ion Concentration to Problems in Rubber Technology. A general summary of the work, alphabetical list of references, and temperature tables complete the book, which is well indexed. The work is valuable for the research chemist interested in latex. [From *India Rubber World.*]

Standard's Year book, 1932. Compiled by The Bureau of Standards. Miscellaneous Publications No. 133. United States Government Printing Office, Washington, D. C.

Subjects covered in this book range from accident prevention to zoning systems and include references to important work having a direct bearing on reducing the cost to the public and increasing the profit of manufacturers of a wide range of articles. A number of references are made to specifications, testing, and other features of manufactured rubber. The first section of the book, a symposium on standardization in communication, is one of the most interesting features of the book. The section on national and international standardizing agencies contains information collected from all the original sources, almost impossible to find elsewhere than in this year book. [From *India Rubber World.*]

Hoyer-Kreuter Technical Dictionary. Sixth Edition. Three volumes; three languages; 2295 pp. Published in Germany; sole agent in the United States, The Industrial Press, 148 Lafayette St., New York City. Price, for the three volumes, $55; for two volumes, $37.50; for one volume, $19.50. 1932.

The Hoyer-Kreuter Technical Dictionary has been published in a new and enlarged edition including 100,000 carefully selected technical terms embracing various industries, arts, and sciences. This colossal work is in three large volumes: German-English-French; English-German-French; and French-German-English. Volume 1 has the German words alphabetically arranged, with definitions following in both English and French; Volume 2 has English entry words, with definitions in German and French; and Volume 3, French entry words. The technical elements of the three languages thus become interchangeable [From *The Rubber Age* of New York.

[Contribution from the Rubber Research Scheme, Ceylon, published in The Tropical Agriculturist, Vol. 76, No. 6, pages 342–344, June, 1931.]

The Cause of Variability in the Plasticity of Plantation Rubber after Storage

G. Martin and L. E. Elliott

Of the Scientific Staff in London of the Ceylon Rubber Research Scheme

There are two reasons why a study of the plasticity of rubber is of importance to the planter, *viz.*: (1) the variable plasticity of plantation rubber leads to many difficulties in manufacturing operations; and (2) first-grade plantation rubber is so hard that it is frequently mixed with inferior grades and other materials to enable it to pass more easily through the different processes.

The results of the investigations recorded in this report suggest a definite reason for the hardness and variability of first-grade rubber.

Tests carried out by De Vries in Java showed: (1) that freshly prepared plantation rubber is uniform in plasticity, but that many samples gradually become hard or soft on keeping and so develop differences; and (2) that rubber containing more serum substances than usual becomes hard, and that containing less than usual becomes soft.[1] On the other hand, tests carried out by the Scheme on a large number of samples for over three years show that in most cases rubber becomes harder on keeping for six months at 15° C. The hardening of the rubber at European temperatures has been confirmed by Griffiths of the Dunlop Rubber Co., Ltd., who stated that large-scale experiments on rubber from different estates showed that in all cases, after storage for three years, it was necessary to increase the time of milling by about 30 per cent in order to obtain the required plasticity.[2]

As raw rubber is subjected to a wide range of temperatures and humidity conditions before use by the manufacturer, a detailed investigation is being carried out at the Imperial Institute on the effect of different conditions of storage.

The results of preliminary tests[3] showed that: (1) rubber becomes slightly harder at 15° C. than at 0° C.; and (2) rubber hardens more quickly in a dry than in a damp atmosphere. Further experiments have now been made with crepe and sheet stored for six months at 0°, 30°, and 45° C. As it was desirable to ascertain whether the changes in plasticity were due to changes in the rubber, independent of external factors such as oxygen, some of the samples were kept in sealed glass tubes containing dry nitrogen and others in tubes containing dry oxygen. If oxygen is responsible for changes in the plasticity of rubber on storage, it might be anticipated that the changes would be accelerated by the removal of antioxidants from the rubber. Accordingly, a portion of the sheet was treated with dilute ammonia solution for three weeks to remove antioxidants; another portion was treated with water for comparison; and a third with tannic acid solution, the tannic acid being regarded as a possible antioxidant. The results of the usual hardness tests at 100° C. are shown in the following table and diagrammatically in Fig. 1.

The results show that the changes in hardness which occur when rubber is stored in dry oxygen are different from those which occur on storage under the same conditions in nitrogen. In nitrogen the rubber becomes hard and the hardness increases with the temperature. In oxygen the rubber is always softer than in

nitrogen at the same temperature, and the difference increases with the temperature.

These results suggest that two fundamental factors are responsible for the changes which occur in the plasticity of rubber on storage: (1) a spontaneous hardening which occurs in nitrogen and therefore probably in any inert atmosphere; and (2) a softening induced by oxygen. These changes occur simultaneously when oxygen is present, but an increase in temperature accelerates the rate of softening more than the rate of hardening. At low temperatures hardening exceeds softening and at high temperatures softening exceeds hardening, and, as will be seen from the diagram, the critical temperature is about 30° C., but depends upon accessory substances in the rubber.

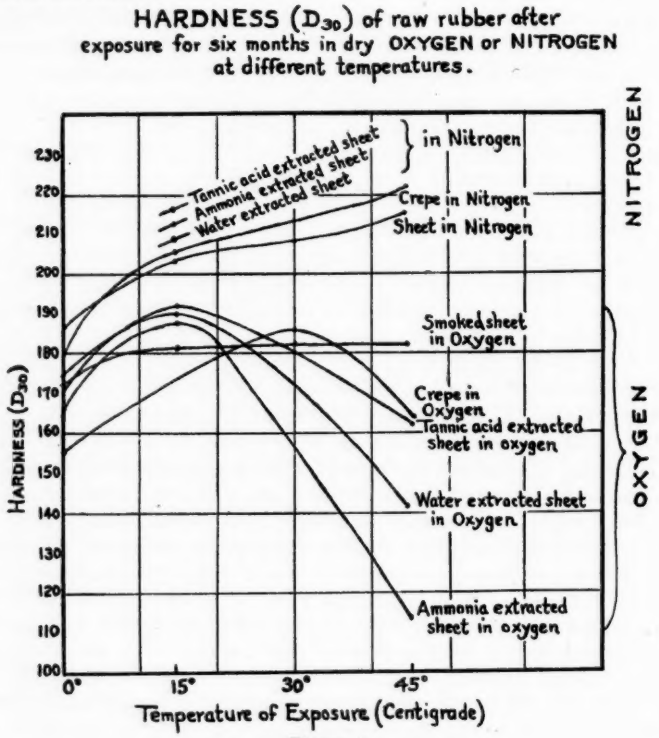

Figure 1

The ammonia-extracted rubber became extremely soft in oxygen at 45° C., although it hardened at 15° C., while the same rubber not treated with ammonia had a tendency to harden even at 45° C. Previous experiments with ammonia-extracted rubber have indicated that it possesses poor aging properties when vulcanized, and it is assumed that this is due to the removal of antioxidants.[4] The removal of these components, therefore, appears to affect not only the aging properties of the vulcanized material but also those of the raw material.

The water-extracted rubber also softened in oxygen at 45° C., but not as much as the ammonia-extracted rubber; this also agrees with the results of the aging tests on the vulcanized material referred to above. Tannic acid does not appear to have a marked antioxidant effect.

These results explain the differences previously observed between the effect of storage in the tropics and in Europe. At European temperatures spontaneous hardening nearly always exceeds softening due to oxygen, even when the amount of antioxidants present is much less than usual. At tropical temperatures rubber becomes hard or soft according to the amount of serum substances present. These

Sample	* D_{30} (Mm./100) before Storage	*D_{30} (Mm./100) after Storage for Six Months in Dry Nitrogen at 0°	15°	30°	45°	Dry Oxygen at 0°	15°	30°	45°
Crepe	170	178	205	213	222	156	173	185	164
Smoked sheet	191	186	203	208	215	173	183	182	182
Smoked sheet extracted with cold water	189	...	209	...	...	175	188	...	142
Smoked sheet extracted with ammonia	189	...	213	...	...	166	186	...	111
Smoked sheet soaked in tannic acid	189	...	217	...	...	170	191	...	162

* D_{30} = Thickness (in hundredths of a millimeter) of sphere 0.4 gram in weight after pressing under a load of 5 kg. at 100° C. for 30 minutes.

contain natural antioxidants, with the result that even at tropical temperatures rubber containing more serum than usual becomes hard.

Although this work is only in its initial stage, the results indicate methods by which it may be possible to control the plasticity of rubber on estates.

References

[1] *Trans. Inst. Rubber Industry*, **3**, 284 (1927–1928).
[2] *Trans. Inst. Rubber Industry*, **3**, 300 (1927–1928).
[3] *Second Quarterly Circular of the Rubber Research Scheme*, Ceylon, **1930**.
[4] *Trans. Inst. Rubber Industry*, **2**, 368 (1926–1927).

[From Transactions of the Institution of the Rubber Industry, Vol. 7, No. 3, pages 196–208, October 1931.]

The Absorption of Water by Rubber and Its Relation to the Protein Content

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Object of the Investigation

The proportion of water in samples of rubber has long been noted as a variable factor, but attempts do not appear to have been made to relate this factor to the composition of the rubber.

It was therefore decided to determine whether any relation existed between the proportion of water absorbed by, and the protein content of, the rubber.

Introduction

Whitby (*J. Soc. Chem. Ind.*, **37**, 278T (1918)) and Van der Leur (*Mecled, Delft*, **1916**, 473) have shown that crepe and sheet rubber absorb water on increasing the humidity of the air in contact with the rubber.

Whitby concludes, first, that the percentage of moisture in raw rubber in the form of crepe or sheet varies considerably with the degree of humidity of the surrounding air; second, that sheet tends to retain a higher percentage of moisture than crepe rubber; and third, that the moisture-retaining capacity of raw rubber is closely associated with the presence of serum solids. The latter are very hygroscopic.

Van Rossem (*J. Soc. Chem. Ind.*, **1917**, 1104) states that many analyses of first-latex rubber show that sheets have a higher moisture content than crepes. Apart from the probable effect of hygroscopic components in the rubber originating from the latex, it is shown by Van Rossem that the hygrometric state and temperature of the atmosphere also influence the absorption and retention of moisture. Rubber exposed to saturated air at 30° C. takes up a greater quantity of moisture than rubber under the same conditions at 16° C. He states that when the moisture in the air is below 85 per cent of the maximum quantity, the absorption is much reduced.

Method of Procedure

The present work has been concerned with raw rubber, and in most cases the samples were various kinds of crepes.

(*a*) *Shredding.*—The samples were first shredded by passing them through a mill with one roller held stationary. Shredding was found necessary for the following reasons: (1) To ensure that each sample exposed as nearly as possible the same surface area to the moist air, (2) to diminish the time necessary for equilibrium to be established in the various atmospheres, and (3) unshredded samples gave false equilibrium values due to very slow absorption. For example, a sample of blanket crepe from native rubber, when suspended in a jar over air of 94.9 per cent humidity, contained after four days 1.7 per cent of moisture, whereas a shredded sample of the same rubber had absorbed 3.1 per cent of water in the same time. The unshredded sample was gaining water so slowly that it appeared

to be at equilibrium. After a further period of 72 hours it had gained only 0.10 per cent by weight.

(*b*) *Method of Drying the Samples.*—After shredding, the samples were placed in desiccators over concentrated sulfuric acid for 72 hours. This time was insufficient to dry the rubber completely, but it was effective in removing any surface moisture. As it was impossible to dry all the samples at once, they were treated in two batches, and the results for each group were kept separately as Series A and B.

(*c*) *Estimation of Residual Moisture.*—Each sample after treatment as above appeared to retain a proportion of volatile substances, which were only removed on heating in a steam oven for approximately 2 hours. The exact nature of these substances appears to be still uncertain, but it is probable that moisture is the predominating component. Dawson and Porritt (*Trans. Inst. Rubber Industry*, **2**, 345 (1927)) have shown that formic acid and carbon dioxide are present in the vapor obtained by passing air over rubber at room temperature, and it appears probable that the loss in weight on heating may be attributed, at least in part, to the formation of these substances. Armstrong and Drakeley (*Analyst*, **52**, 338 (1927)) showed that on allowing rubber to dry in a vacuum desiccator over pure sulfuric acid, and calculating the amount of moisture present from the loss in weight, a lower result was obtained than when the same rubber was heated in a steam oven at 95°–99° C. This appears to indicate that a proportion of the volatile material termed "residual moisture" is probably formed from oxidation of the rubber, or some component. For the purposes of nomenclature in this investigation, the loss in weight on heating has been termed residual moisture.

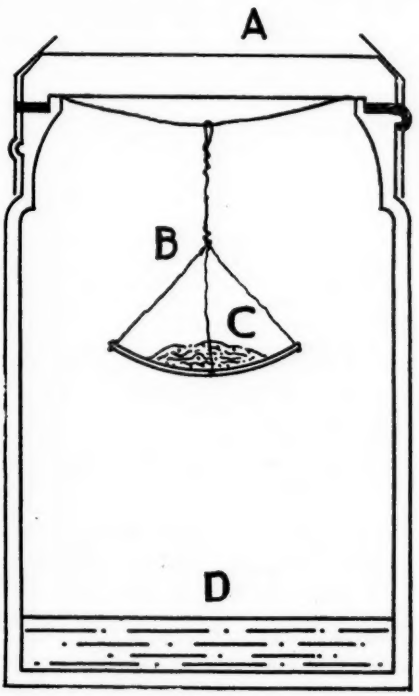

Figure 1

A. Air-tight stopper C. Watch glass and sample
B. Aluminum wire D. Sulfuric acid solution

(*d*) *Calculation of the Percentage of Protein.*—In order to obtain the percentage of protein from the percentage of nitrogen it was necessary to use a factor. The generally accepted factor is 6.25, but doubt has been thrown on its accuracy; it is based on the assumption that the proteins present in the rubber contain 16 per cent of nitrogen, and also that the nitrogen present is all there as protein. Analysis of the common proteins shows that the content of nitrogen varies from 15–17 per cent and hence 16 per cent can be taken as a fair figure, which reduces errors to the minimum possible. Fickendy (*Kolloid-Z.*, **8**, 43 (1910)) pointed out that *Funtumia* latex contains peptones, and showed that it was coagulated by peptone precipitants. Van Rossem (*J. Soc. Chem. Ind.*, **36**, 1105 (1917)) showed

that on extracting rubber with distilled water, the extract contained nitrogen. Van Rossem and Dekker (*J. Soc. Chem. Ind.*, **36**, 1105 (1917)), working on the so-called insoluble portion of rubber, found that on extraction with petroleum or acetone the extract contained up to 10 per cent of nitrogen.

The latter results indicate that all the nitrogen present in the rubber is not there as protein, but in the absence of a better figure 6.25 has been used throughout for the purpose of calculation. The error introduced will be approximately the same for each sample, and so it should not affect the relative results.

(*e*) *Loss of Moisture by the Rubber.*—As noted previously the time given for the samples to stand over concentrated sulfuric acid was insufficient to give complete dryness, the samples retaining up to 0.2 per cent of moisture. Even after 10 weeks' drying a sample of first quality pale crepe rubber still retained 0.05 per cent of moisture, and a further week's treatment had no appreciable effect.

The analytical results are given in Table I, and, as will be observed, the tendency is for rubbers with high protein content to retain less moisture than those with a lower content.

TABLE I

Sample	Percentage of Nitrogen	Percentage of Protein	Percentage of Ash	Percentage Residual Moisture	Percentage Soluble in Acetone
Series A					
Pale crepe I	0.25	1.56	0.35	0.154	1.94
Brown crepe	0.313	1.96	0.62	0.187	2.13
Blanket crepe from native rubber	0.368	2.3	1.17	0.19	1.72
Para rubber	0.86	5.37	0.57	0.065	4.72
Series B					
Pale crepe III	0.185	1.15	0.41	0.186	1.6
Blanket crepe	0.46	2.87	0.34	0.162	3.62
Massai rubber	0.63	3.94	1.31	0.157	6.22
Lahon sheets	0.837	5.23	0.75	0.067	5.49

(*f*) *Water Absorption Measurement.*—To obtain atmospheres of known humidities, small quantities of sulfuric acid solutions of various specific gravities were placed in air-tight jars. From the specific gravities of the solutions, the humidities of the air in the jars obtained from the tables compiled by Hepburn (*Proc. Phys. Soc.*, **40**, 5 (1928)).

It was decided that the measurements should be carried out at 25° C., and this temperature was maintained by means of an electrically controlled oven.

Determinations of the water absorption were made at six different humidities. The humidities and strength of the acid solutions are given in Table II.

TABLE II

Percentage of acid	40.93	35.71	31.11	26.04	20.91	10.90
Specific gravity of acid	1.310	1.265	1.225	1.185	1.145	1.070
Percentage humidity at 25° C.	58.5	67.7	75.3	82.6	88.6	94.9

The samples were suspended in the jars on watch glasses supported by stirrups of aluminum wire. It was at first proposed to use copper stirrups, but in view of the known deleterious action of copper when in contact with rubber, aluminum was chosen. The latter metal had no visible effect on the samples.

The method of suspension is illustrated in Fig. 1, and is similar to that suggested by the Research Association of the British Rubber Manufacturers.

It had been proposed to control the humidity by means of saturated solutions of salts such as sodium chloride, potassium chloride, and potassium sulfate. As, however, the data available regarding the humidities over solutions of these and other salts did not appear to be sufficiently detailed, the acid method was adopted.

At first trouble was experienced owing to water evaporating from the solutions and condensing on the rubber. This was traced to slight variations in the temperature in the oven, and upon precautions being taken to prevent this, no further difficulty was experienced.

Time of Absorption

To determine the rate of absorption of water by the rubbers, five samples were first dried in the desiccator for four days, heated to constant weight in a steam

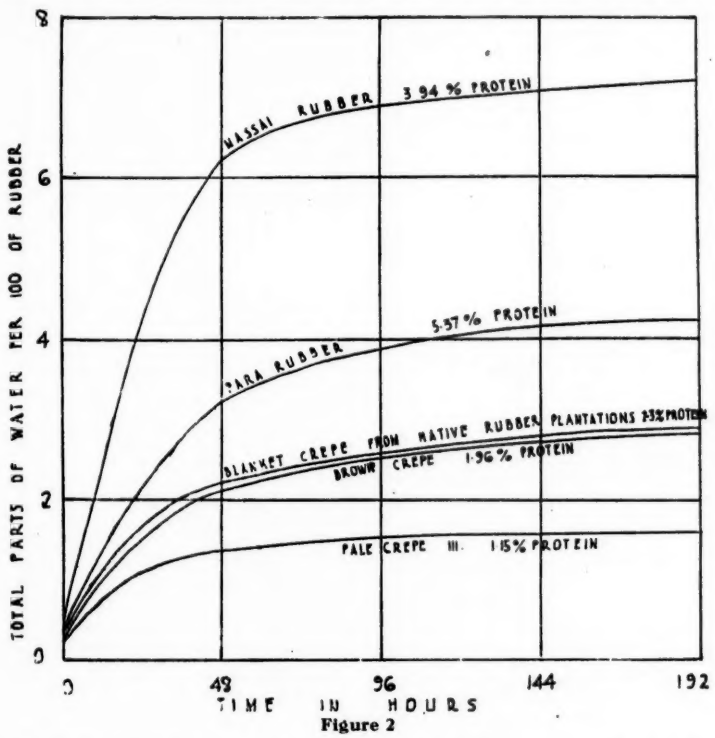

Figure 2

oven, and similar samples were placed in the air-tight jars over sulfuric acid, giving a humidity of 94.9 per cent at 25° C.

TABLE III

ABSORPTION OF WATER BY 100 PARTS OF RUBBER

Sample	24 Hours	48 Hours	120 Hours	144 Hours	168 Hours	Percentage Residual Moisture
Pale crepe III	1.01	1.2	1.4	1.4	1.4	0.13
Brown crepe	1.56	1.91	2.44	2.53	2.55	0.18
Blanket crepe from native rubber	1.62	1.95	2.50	2.55	2.60	0.17
Massai rubber	4.50	5.8	6.2	6.6	6.6	0.48
Para rubber	2.5	3.0	3.8	3.9	4.0	0.22

The samples were weighed at periods of 24 hours for six days and the results are given in Table III.

The results given in Table III are illustrated in Fig. 2, from which it will be observed that equilibrium conditions will be attained in approximately one week. In all subsequent experiments not less than one week was allowed for equilibrium to be established.

It will also be observed that, with the exception of Massai rubber, the curves are in order of their respective protein contents.

The total weight of water in 100 parts of rubber at equilibrium with the various atmospheres is given in Table IV.

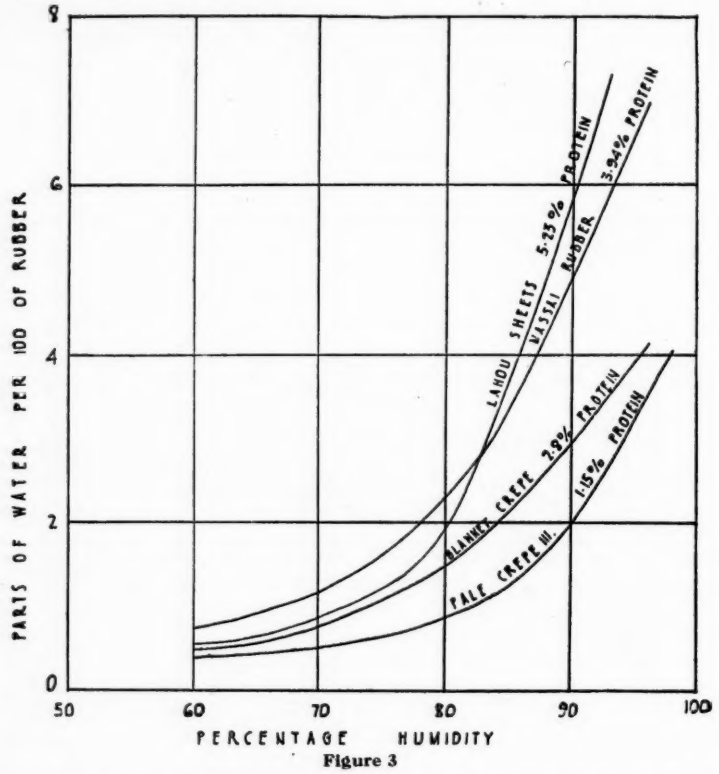

Figure 3

The results given in Table IV are illustrated in Figs. 3 and 4. It will be observed that at the lower humidities the total water content appears to bear no relation to the protein content of the rubbers; this is probably due to the small absorption and to the slow attainment of equilibrium, and also to unavoidable inequalities in shredding. At humidities exceeding 80 per cent the curves assume the expected order (*cf.* Van Rossem, *J. Soc. Chem. Ind.*, **1917,** 1104), and show that the total water content increases with increasing protein content. It is, however, to be observed that the results are plotted in two separate figures for the series A and B. This is due to the fact that if the series are combined, the observed relationship does not entirely hold, the outstanding exception to the rule being the sample of Massai rubber.

A similar discrepancy may be observed in Fig. 2, in which the Massai rubber again occupies an unexpectedly high position in the graph.

It may be that this sample contains a high percentage of the serum components of the latex and these, being very hygroscopic (*loc. cit.*), mask the effect of the protein content.

The latter contention is supported by the results obtained using a sample of sprayed latex rubber; this latter sample contained 3.9 per cent of protein, and yet absorbed 20 parts of water per 100 of rubber. The content of serum solids is undoubtedly the main factor to which this high absorption may be attributed.

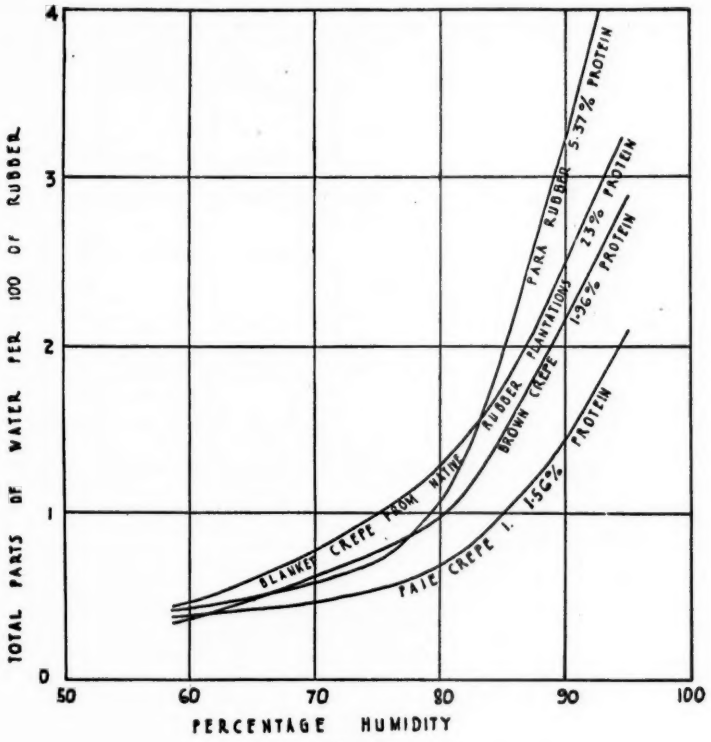

Figure 4

TABLE IV

TOTAL WATER ABSORPTION PER 100 PARTS OF RUBBER

Sample	Humidities (Per Cent)					
	58.5	67.7	75.3	82.6	88.6	94.9
Pale crepe I	0.35	0.45	0.57	0.80	1.25	2.10
Brown crepe	0.34	0.54	0.75	1.15	2.08	2.88
Blanket crepe from native rubber	0.42	0.72	0.99	1.49	2.49	3.29
Para rubber	0.40	0.57	0.67	1.47	2.97	4.27
Pale crepe III	0.32	0.53	0.73	1.02	1.28	2.48
Blanket crepe	0.42	0.72	1.09	1.8	2.68	..
Massai rubber	0.74	1.04	1.68	2.75	4.45	6.65
Lahon sheets	0.58	0.87	1.08	2.67	..	..

It was, however, observed that if the absorption of water were related to the residual moisture in each sample of rubber, the curves of each series actually appear in order of their protein content. In Table V the absorption is expressed as the ratio of the water taken up by the rubber to the residual moisture retained by the rubber after drying over sulfuric acid. Fig. 5 shows the results graphically, from which it will be seen that the higher the protein content, the greater the ratio of absorption for all rubbers tested.

Similarly, if the figures obtained for the absorption of water by each sample at various humidities (see Table VI), are taken and expressed as the rate of water absorbed to residual moisture (Table VII), results are obtained which show in

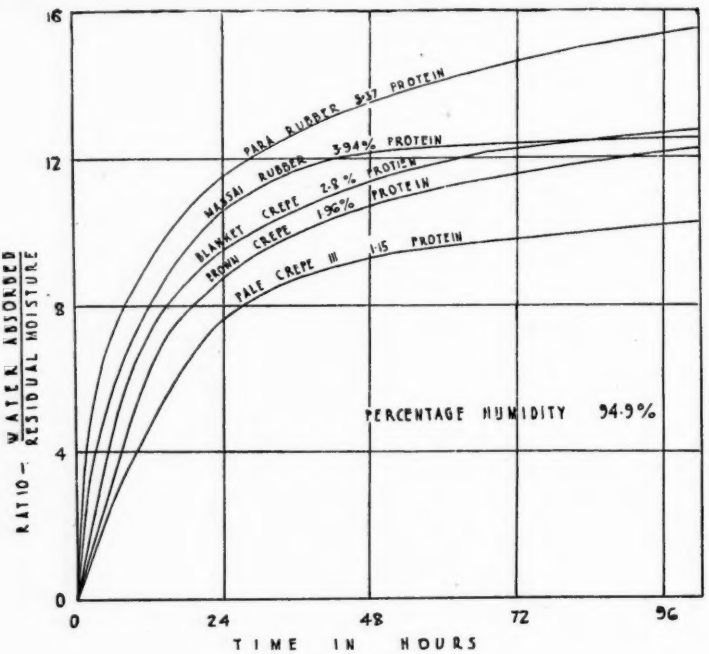

Figure 5

TABLE V

RATIO: $\frac{\text{WATER ABSORBED PER 100 PARTS OF RUBBER}}{\text{PARTS RESIDUAL WATER PER 100 RUBBER}}$

Sample	Time in Hours				
	24	48	120	144	168
Pale crepe III	7.7	9.2	10.7	10.7	10.7
Brown crepe	8.7	10.6	13.6	14.0	14.1
Blanket crepe from native rubber	9.5	11.2	14.2	15.0	15.3
Massai rubber	10.4	12.1	12.9	13.75	13.75
Para rubber	11.4	13.6	17.3	18.2	18.2

Humidity of air = 94.9 per cent. Temperature 25° C.

every instance the increase in the ratio, both with rising protein content and also with rising humidity. These results for series B are illustrated graphically in Fig. 6. Series A will give a similar graph.

TABLE VI

WATER ABSORBED PER 100 PARTS OF RUBBER

Sample	Humidity (Per Cent) 58.5	67.7	75.3	82.6	88.6	94.9
Series A						
Pale crepe I	0.20	0.30	0.41	0.65	1.1	1.95
Brown crepe	0.15	0.35	0.56	1.07	1.89	2.69
Blanket crepe from native rubber	0.23	0.53	0.80	1.3	2.3	3.1
Para rubber	0.33	0.50	0.63	1.40	2.90	4.20
Series B						
Pale crepe III	0.13	0.345	0.54	0.84	1.1	2.3
Blanket crepe	0.26	0.56	0.93	1.64	2.52	..
Massai rubber	0.58	0.88	1.52	2.61	4.3	6.5
Lahon sheets	0.51	0.805	1.01	2.6	..	..

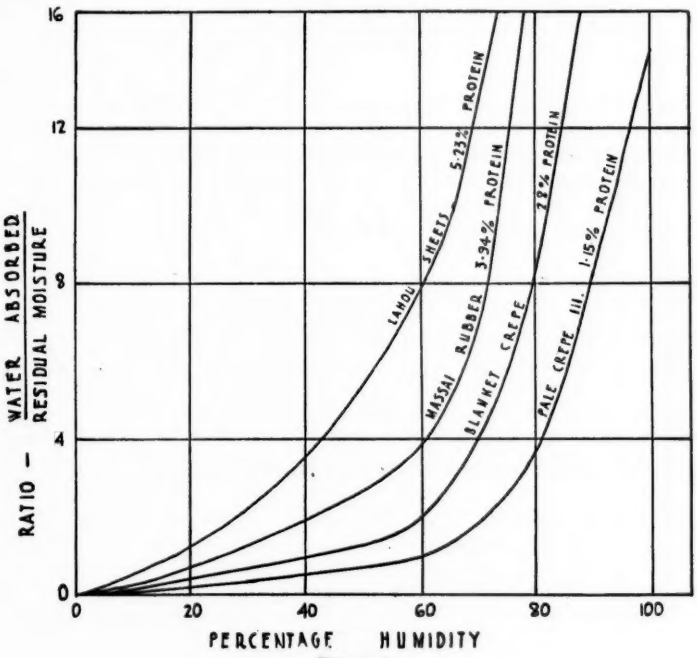

Figure 6

TABLE VII

RATIO: WATER ABSORBED TO RESIDUAL MOISTURE PER 100 PARTS OF RUBBER

Sample	Humidity (Per Cent) 58.5	67.7	75.3	82.6	88.6	94.9
Series A						
Pale crepe I	1.1	1.8	2.7	4.2	7.1	12.0
Brown crepe	0.8	1.87	3.0	5.72	10.1	14.4
Blanket crepe from native rubber	1.2	2.8	4.2	6.8	11.2	17.0
Para rubber	5.1	7.7	9.7	21.5	44.6	64.6
Series B						
Pale crepe III	0.7	1.9	2.9	4.5	6.0	13.4
Blanket crepe	1.6	3.4	5.74	10.1	15.5	..
Massai rubber	3.7	5.6	9.7	16.5	27.5	41.5
Lahon sheets	7.6	12.0	15.1	38.8	..	..

TABLE VIII

Sample	Humidity (Per Cent) 50	60	70	80	90
Series A					
Pale crepe I	0.6	1.0	1.8	4.0	8.6
Brown crepe	0.2	1.0	2.2	4.6	10.7
Blanket crepe from native rubber	0.6	1.4	3.0	5.7	12.0
Para rubber	3.4	5.4	8.0	16.0	..
Series B					
Pale crepe III	0.4	0.8	2.0	3.9	6.7
Blanket crepe	0.95	1.80	4.0	8.2	16.6
Massai rubber	2.65	3.9	6.4	13.4	..
Lahon sheets	5.4	8.2	13.1	..	..

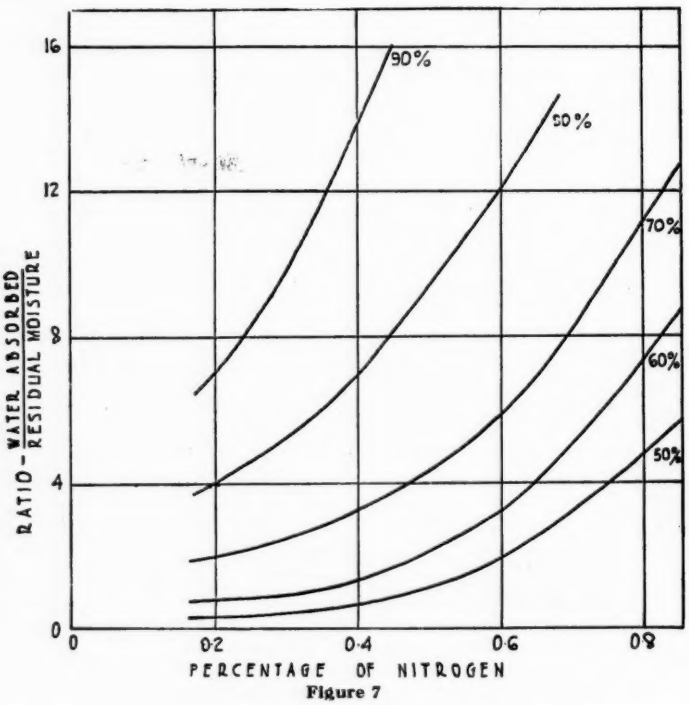

Figure 7

From the figures it is possible to obtain the value for the ratio at humidities of 50, 60, 70, 80, and 90 per cent, and these figures are given in Table VIII for both series.

These results are illustrated graphically in Fig. 7 for series B (series A gives similar results) and show that as the protein content increases there is a steady increase in the ratio of the water absorbed to the residual water in the rubber for all humidities.

It will be observed that the nitrogen content in the samples varied from 0.185 per cent to 0.86 per cent and the corresponding protein content from 1.15 per cent to 5.57 per cent. The rubbers did not appear abnormal in any way except that in a few instances, *e. g.*, in Massai rubber and blanket crepe from native rubber planta-

tions, a high ash content was noted. However, it appears improbable that this factor has had any serious effect on the water absorption.

It is, of course, essential that as the samples were dried in two batches under different conditions, the results for each group should be kept separate when the ratio, water absorbed to residual moisture, is considered.

Determinations of the protein content of smoked sheet rubber have given results of approximately 2.5–3.0 per cent, whereas pale crepe contains about 2 per cent protein. Hence it would be anticipated that sheet would contain more moisture than crepe rubber. This statement has been verified, and agrees with the conclusion of Whitby, Van der Leur, and Van Rossem (*loc. cit.*).

The absorption of water by vulcanized samples is now under investigation.

Conclusions

1. The absorption of water by rubber is dependent upon the degree of division, and comparable results are obtained in a reasonable time only by using shredded samples of rubber.

2. The moisture in rubber appears to be present in two forms, (*a*) that removed after, say, three days, over sulfuric acid, and (*b*) what has been termed the residual moisture, which is more difficult to extract from the rubber, but which is evolved by heating the sample for an hour or so at 100° C. In general, the higher the protein content the lower the percentage of residual moisture.

3. Solutions of sulfuric acid provide suitable means of adjusting the humidity of the air.

4. The temperature must be kept constant to avoid deposition of dew upon the rubber.

5. The rate of absorption of moisture decreases rapidly after the first 24 hours of exposure to the prescribed atmosphere. The absorption after 5 days is very slow, and equilibrium was attained in approximately one week.

6. In general the rate of absorption is higher with rubbers containing a large percentage of protein matter. The rate of absorption in an atmosphere of humidity of less than 80 per cent is slow, and for experimental purposes a humidity of approximately 95 per cent is shown to be suitable.

7. It has been found that the ratio of the water absorbed at a constant humidity to the residual moisture is in all cases related to the protein content.

8. In general, the total weight of water absorbed per 100 parts of rubber rises with rising protein content provided the humidity of the air in contact with the rubber is 85 per cent or higher.

9. The proportion of moisture absorbed in atmospheres of less than 70 per cent humidity is small, but increases rapidly with increasing humidity.

[From Transactions of the Institution of the Rubber Industry, Vol. 7, No. 3, pages 254–271, October, 1931.]

Experiments on the Electrodeposition of Rubber from Latex

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Freshly tapped latex contains on the average from 27 to 35 per cent of rubber and from 1.2 to 1.7 per cent of acetone-soluble matter, such as resin and water-soluble sugars, from 1.5 to 2.0 per cent of protein and 0.25 to 0.20 per cent of mineral matter. The last consists mainly of the phosphates of calcium, magnesium, and potassium, with organic salts of these metals and a small amount of sulfate. Doubts have been expressed as to the existence of rubber as such in latex, since the physical properties of the dispersion bring it within the category of emulsions, *i. e.*, of dispersions whose dispersed phase is liquid. Thus it has been suggested that the dispersed particles must consist of some simpler hydrocarbon which is polymerized to rubber during coagulation. From results obtained with the micro-manipulator, Freundlich and Hauser (*Kolloid-Z.*, **36,** 75 (1925)) concluded that the particles in latex consist of an elastic (solid) outer skin containing a viscous liquid, and assumed that the inner liquid hydrocarbon and the outer solid represent different stages of polymerization of the basic hydrocarbon isoprene C_5H_3. It is, of course, quite probable that the ejection of liquid which these investigators observed when a latex particle is punctured resulted from the rupture by the needle of the field of force at the surface of a liquid particle, and it is perhaps advisable to adhere to the more conservative conclusion of Stamberger ("The Colloid Chemistry of Rubber" (1929)) that in all raw rubber dispersions we are mainly concerned with liquid disperse phases. Latex is a relatively coarse dispersion with an average particle size of 0.5μ, and the particles vary in size from 2.0 to 0.1μ, *i. e.*, from microscopic to ultra-microscopic particles (von Weimarn, *Kolloid-Z.*, **46,** 217 (1928)).

It is maintained by Stamberger (*loc. cit.*) that latex is a lyophobe system because of the readiness with which the dispersed particles can be separated from the serum by gravitation or by altering the charge with electrolytes. Because of the strong affinity between the dispersed phase and the dispersion medium in a lyophile sol, the particles are heavily hydrated, *i. e.*, are surrounded by a film of water which acts as an additional stability factor. As coagulation experiments give evidence of the existence of this other stability factor, latex has been described (De Vries, *Archief*, **8,** 233 (1924); Beumée-Nieuwland, *Ibid.*, **13,** 555 (1929)) as a lyophile system, the lyophile properties being attributed to a layer of protein adsorbed on the rubber particles. The most recent view (van Harpen, "The Electrometric Determination of the Hydrogen-Ion Concentration in Latex of Hevea Brasiliensis and Its Applicability to Technical Problems" (1930)) makes a compromise in describing latex as a pseudo-lyophile dispersion, thereby expressing the idea that materially a lyophobe colloid is present, but that several properties of the dispersion are those of a lyophile colloid.

In any dispersion the dispersed particles acquire an electric charge relative to the dispersion medium. V. Henri (*Le Caoutchouc et la Gutta-Percha*, **3,** 513 (1906)) was the first to observe that in rubber latex the dispersed particles have a negative charge, and that under the influence of an electric field they move toward the anode or positive pole. This migration, which is technically known as electro-

phoresis, renders possible the manufacture of rubber articles by electrodeposition. In the present paper it is intended to give an account of some experiments on the mechanism of electrophoresis in latex, and an indication of the various factors affecting the nature of deposits obtained thereby. Owing to the commercial issues involved, it will not be possible to deal with many aspects of the problem; the aim is to indicate the general methods employed in the necessary research work rather than to discuss in detail the results obtained.

Variability of Preserved Latex

Owing to its instability, latex can only be transported when either an alkaline substance or an antiseptic has been added as a preservative. Of such substances, formaldehyde, soaps, ammonia, and the carbonates and hydroxides of the alkali metals are most frequently used. The technical difficulties of electrodeposition are often enhanced by variation in physical and chemical properties of successive deliveries of preserved latex.

The following values of the physical constants obtained with samples of the same preserved latex supplied at different times demonstrate the variations encountered.

TABLE I

PHYSICAL PROPERTIES OF VARIOUS SAMPLES OF A PRESERVED LATEX CONTAINING 15% OF DRIED RUBBER

Sample	Specific Conductance at 25° C. (Mhos × 10^3)	p_H Value
A	5.25	9.9
B	4.69	10.2
C	4.82	7.9
D	4.98	10.1
E	5.19	9.9
F	5.07	9.8

The conductivities were determined by the Wheatstone bridge method, each value given being the mean of four determinations. For the determination of p_H values the Wulff tester was used (Hauser, "Colloid Chemistry of the Rubber Industry" (1928); Mackay, *India Rubber J.*, **79**, 353 (1930)).

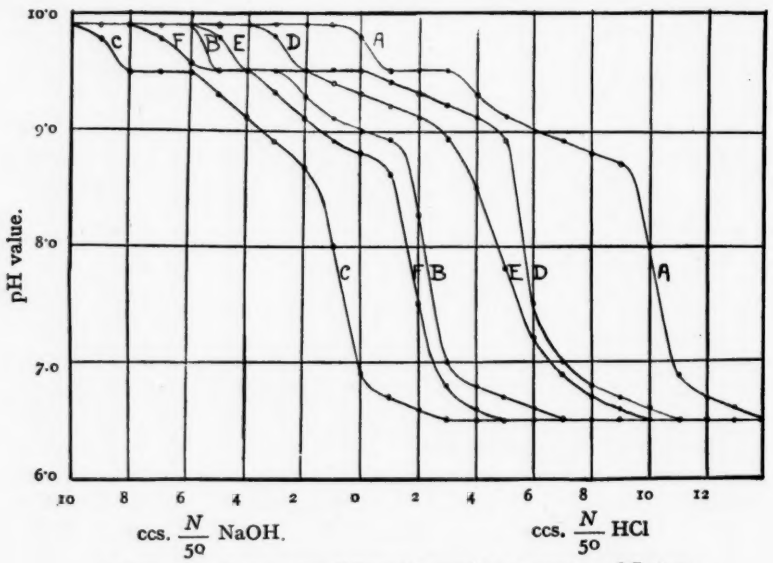
Any substance which shows resistance to change in p_H value on dilution or on addition of acids or alkalies is said to act as a buffer. Buffering power is always a characteristic of salts of weak acids with strong bases, and some components of preserved latices fall into this category as, for instance, many protective colloids (proteins, soaps) and alkaline carbonates. Consequently, it is frequently necessary to estimate the buffering power of preserved latices. The procedure is as follows: 10-cc. portions of the preserved latex (diluted to 15 per cent rubber content) are pipetted into 50-cc. graduated flasks. Increasing volumes of 0.02 *N* HCl are then run into successive flasks and the volume in each case made up to 50 cc. with distilled water. The acid has to be added slowly to prevent premature local coagulation. The p_H value of each dispersion is then determined by means of the Wulff tester. The effect of adding increasing volumes of 0.02 *N* NaOH is similarly studied.

The results obtained with samples A–F are represented in Fig. 1 and afford further indication of the varations encountered in the raw material.

The Mechanism of Electrodeposition

Cataphoresis in latex may be accompanied by electrolysis of the salts in the serum. The cations most frequently present in preserved latex are those of ammonium

and the alkali metals; when these are discharged secondary reactions occur, *e. g.*, $Na + H_2O \rightarrow [H] + NaOH$, and alkalinity develops around the cathode with evolution of hydrogen. Similarly, unless the ions arriving at the anode form readily ionizable salts with the metal of the anode, secondary reactions again take place, *e. g.*, $SO_4'' + H_2O \rightarrow H_2SO_4 + [O]$, and acidity develops around the anode, with formation of oxygen. In the atomic state, the oxygen may combine with the depositing rubber and yield an inferior product; in the molecular state it will pass into and through the fresh rubber deposit, thereby rendering it spongy and porous. Much of the patent literature is concerned with overcoming this difficulty and many means have been suggested, such as the insertion of a porous diaphragm in front of the anode (Anode, E.P. 223,189, **1923**; Kodak, E.P. 253,091, **1925**; Siemens, E.P. 307,879, **1928**), prior removal by dialysis of electrolytes (especially alkalies) favoring the development of gas (Kodak, E.P.



pH Titration Curves for different samples of preserved Latex each containing 3 per cent. of rubber.

Figure 1

251,979, **1925**; Anode, E.P. 257,885, **1925**; Cowper-Coles, E.P. 291,471, **1926**), the use of metals which ionize continually in conjunction with dialyzed latex (Anode, E.P. 257,885, **1925**); the introduction of reducing agents which will combine with the nascent oxygen (Anode, E.P. 246,532, **1924**; Kodak, E.P. 253,085, **1925**), addition of electrolytes of specifically low decomposition voltages (Anode, E.P. 246,532, **1924**; E.P. 257,885, **1925**), and electrophoresis without electrolysis (E.P. 257,885, **1925**). The efficacy of these expedients need not be considered here, as the present series of experiments have been concerned entirely with the process of W. A. Williams as defined in E.P. 293,095, **1927**; this patent covers the use of two electrodes of the same metal in presence of a salt of that metal; under these circumstances, there is no opposing electromotive force of polarization, and the feeblest current is sufficient to produce electrophoresis; a combination of zinc electrodes in presence of zinc sulfate is usually employed.

It is essential in the process that the anodic material consist of practically pure zinc. For instance, at one time considerable difficulty was experienced in duplicating results in small scale experiments, and we suspected that the electrodes were responsible for the irregularities. Six anodes (A, B, C, D, E, F) were therefore selected, two from each of three deliveries of zinc, and each was used in a bath containing 15 per cent of rubber and $^{7}/_{16}$ per cent of zinc sulfate. Deposits from

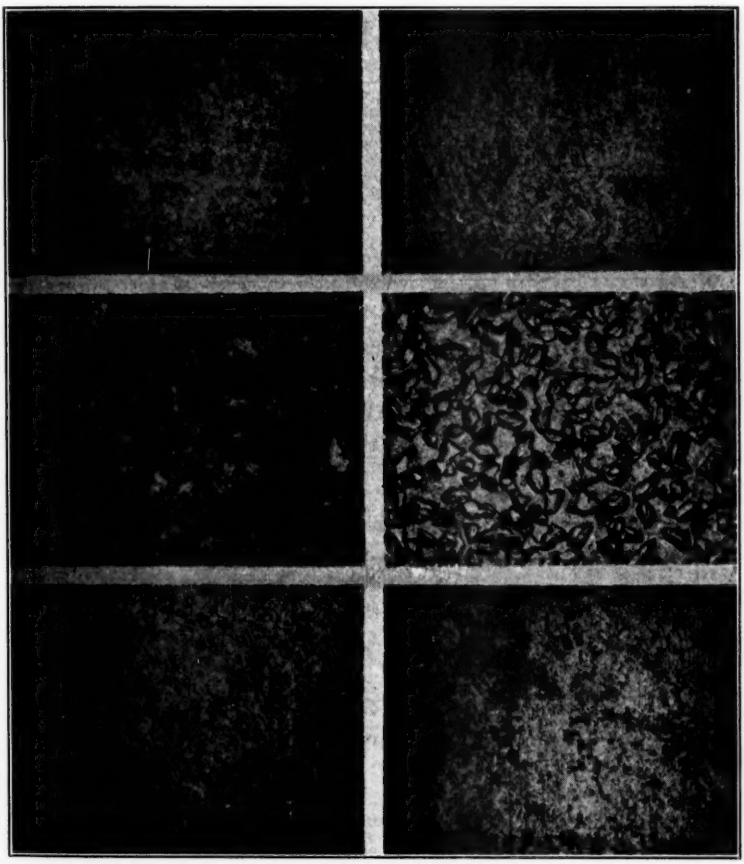


Figure 2—The Effect of Impurity in the Anode Material on the Nature of the Deposit
(Magnification 10×)

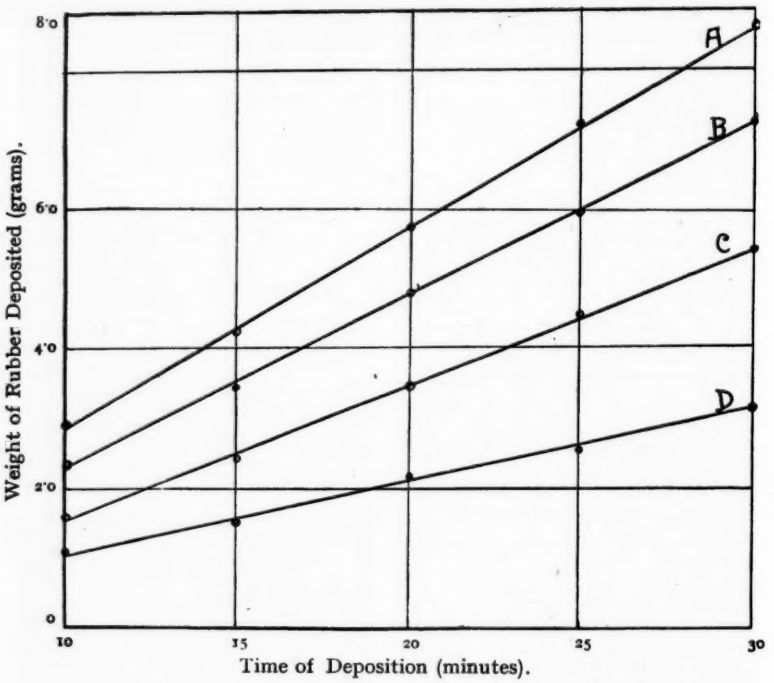
mandrels A, B, E, and F were almost free from defects, whereas those from C and D showed microporosity ("pinheads"), as will be seen from the accompanying photomicrographs (Fig. 2). Qualitative analysis of the material of each anode revealed that A, B, E, and F consisted almost entirely of zinc, whereas C and D contained a readily recognizable proportion of lead. Depositions were then made using the anodes in two baths containing 15 per cent of rubber, $^{5}/_{16}$ per cent of sodium chloride and acetate, respectively. In the first case, the deposits on C

and D again showed "pinheads," whereas all the deposits from the bath containing sodium acetate were of good texture and free from defects.

Since lead chloride and sulfate are sparingly soluble salts, whereas lead acetate dissolves readily in water, these results confirm our view that "pinheads" will be produced whenever conditions favor the formation of a sparingly soluble salt by union of a metal ion from the anode with an anion from the dispersion.

Quantitative Experiments

In most of the experiments deposition from latex mixes was continued for definite periods at definite current densities on flat zinc plates having an active area of 0.25



A 1·0 amps. per sq. dm.; B 0·8 amps. per sq. dm.;
C 0·6 amps. per sq. dm.; D 0·4 amps. per sq. dm.

Figure 3

sq. dm. The moisture contents and dry weights of the deposits were then determined by the following method:

The electrode with the adherent wet deposit was hung to drip for 30 minutes under a bell jar within which also lay a dish of water; the air within the jar was thereby saturated with water-vapor and evaporation of moisture during the dripping stage prevented. The deposit was then transferred from the anode to a weighed clock-glass and weighed while still wet; it was then dried to constant weight at 100° F. Concordant figures were obtained by this procedure.

Factors Affecting the Rate of Deposition

1. *Current Density and Time.*—The weight of rubber deposited on a given area of the anode is approximately directly proportional to the strength of the current

and the time of deposition. This has been verified both by Sheppard (*Trans. Amer. Electrochem. Soc.*, **1927,** 93) and by the present author. The dispersion studied contained 15 per cent of rubber and $^1/_{16}$ per cent of zinc sulfate; results are given in Table II and Fig. 3.

TABLE II

THE EFFECT OF CURRENT DENSITY AND TIME ON THE WEIGHT OF THE DEPOSIT

Current Density (Amp./Dm.^{2})	Time of Deposition (Minutes)	Weight of Dry Deposit (Grams)
0.4	10	1.07
	15	1.49
	20	2.16
	25	2.53
	30	3.13
0.6	10	1.59
	15	2.42
	20	3.44
	25	4.50
	30	5.44
0.8	10	2.34
	15	3.45
	20	4.79
	25	5.94
	30	7.31
1.0	10	2.93
	15	4.25
	20	5.73
	25	7.26
	30	8.72

2. *Concentration of Rubber and Total Conductivity of the Bath.*—McBain and Bowden (*J. Chem. Soc.*, **123,** 2417 (1923)) and Laing (*J. Phys. Chem.*, **28,** 673 (1924)) conducted a series of experiments to show that the phenomena of electrolytic conduction, electro-osmosis, and electrophoresis were but special cases of an inherently identical process. They deduced that for a large colloidal particle, the transport formula would be:

$$n = \frac{cmf}{u},$$

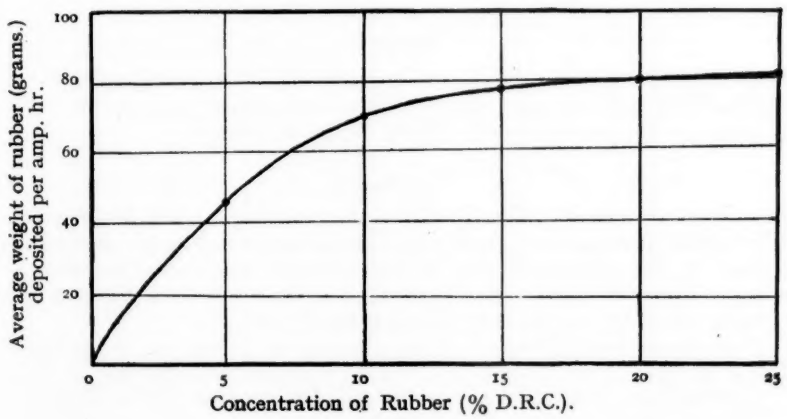


Figure 4

where n is the rate of deposition of the colloidal particle; c, its concentration; m, its ratio of mass to charge; f, its contribution to the conductivity of the dispersion; and u, the total specific conductance of the dispersion. Sheppard (*loc. cit.*) concluded from his experiments that the consequences of this equation were approximately verified, *viz.*, that the quantity of rubber transported per unit of current is directly proportional to the concentration of rubber in the latex and inversely proportional to the total conductivity. The author's experiments yielded similar results; these are shown in Table III and Figs. 4 and 5. Throughout this series the current density was constant (0.60 amp. per sq. dm.) and each bath contained $^1/_{16}$ per cent of zinc sulfate.

The formula of McBain and Laing is only a first approximation so far as rubber is concerned, and the rate of deposition on the anode will be proportional to the

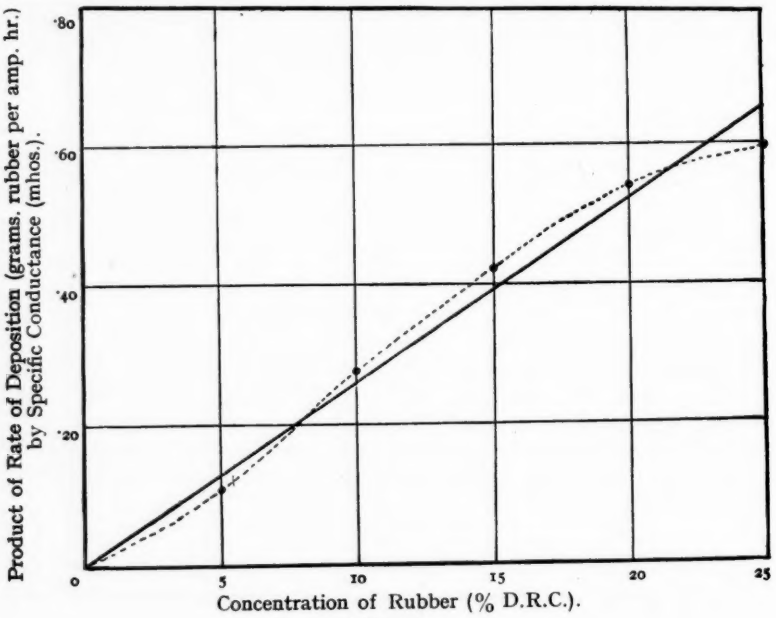


Figure 5

concentration of rubber in the dispersion and to the average migration velocity of the particles given by the formula of Helmholtz (*Wied Ann.*, **7**, 337 (1879)), as modified by Debye and Hückel (*Physik. Z.*, **25**, 49 (1924)):

$$u = \frac{\zeta CD}{6\pi\eta\mu A}$$

where u is the average migration velocity of the particles; ζ, the potential gradient in the double layer of charges at the solid-liquid interface, *i. e.*, the electrokinetic potential; C, the current passing; D, the dielectric constant of the dispersion medium; η, the coefficient of viscosity of the dispersion; A, the active area of the electrodes; and μ, the specific conductance of the dispersion.

Because of the selective nature of the influence of electrolytes on the stability of latex, variations in the magnitude of the electrokinetic potential due to addition of electrolytes are not allowed for by the conductivity factor in the equation of McBain and Laing. Measurements of this contact potential between rubber

TABLE III

RELATIONSHIP BETWEEN RATE OF DEPOSITION, CONCENTRATION OF RUBBER, AND TOTAL SPECIFIC CONDUCTANCE

Concentration of Bath (% D. R. C.)	Time of Deposition (Min.)	Dry Weight of Rubber Deposited (Grams)	Weight of Rubber Deposited per Ampere-Hr. (Grams)	Average Rate of Deposition (Grams per Ampere-Hr.)	Specific Conductance at 25° C. (Mhos × 10^3)	Average Rate of Deposition × Specific Conductance
5	5	0.60	48.0			
	10	1.32	52.8			
	15	1.92	51.2			
	20	2.20	44.0	46.8	2.308	0.108
	25	2.82	45.1			
	30	3.00	40.0			
10	5	0.97	77.8			
	10	1.64	65.6			
	15	2.38	63.4			
	20	3.95	79.0	70.5	3.934	0.277
	25	4.56	72.3			
	30	4.80	64.0			
15	5	1.03	82.4			
	10	1.80	72.0			
	15	2.69	71.7	78.2	5.415	0.424
	20	4.20	84.0			
	25	4.87	77.9			
	30	5.80	77.2			
20	5	1.03	82.4			
	10	1.90	76.0			
	15	2.85	76.0	81.0	6.673	0.541
	20	4.45	88.8			
	25	5.19	83.2			
	30	5.95	79.3			
25	5	1.04	83.2			
	10	1.95	78.0			
	15	2.91	77.6	82.4	7.210	0.594
	20	4.58	91.6			
	25	5.25	84.0			
	30	6.01	80.1			

and water have been made by Ghosh and Stamberger (*Kautschuk*, **5**, 99 (1929)), who measured the electro-osmosis of water in a rubber capillary, and for pure

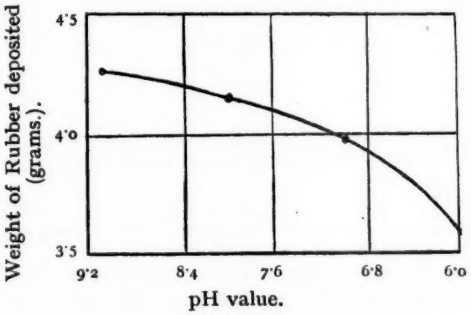


Figure 6

water obtained a value identical with that given by Sheppard (*loc. cit.*), who measured the migration of a boundary layer of the latex with respect to the dispersion medium. In general, the contact potential increases with increased alkalinity, and decreases with additions of cations in proportion to their adsorbability.

Also allowance is not made in the equation of McBain and Laing for variations in the viscosity. Thus Borrowman (*Rubber Industry*, **1911, 243**) has shown that only at concentrations of less than 10 per cent of rubber is there direct proportionality between the viscosity of latex and its concentration; at higher rubber contents the viscosity is relatively greater; the problem is further complicated by Belgrave's statement (*Malayan Agric. J.*, **11, 348 (1923)**) that the addition of even very small quantities of a coagulant produces considerable change in the viscosity of latex.

3. p_H *Value of the Dispersion.*—Since the rate of deposition is proportional to the charge on the particles and this in turn is increased by the addition of alkalies, it would be expected that at higher p_H values more rubber would be deposited. Small scale depositions were made at 0.60 amp. per sq. dm. for 30 minutes from baths containing 15 per cent of rubber to which had been added increasing amounts

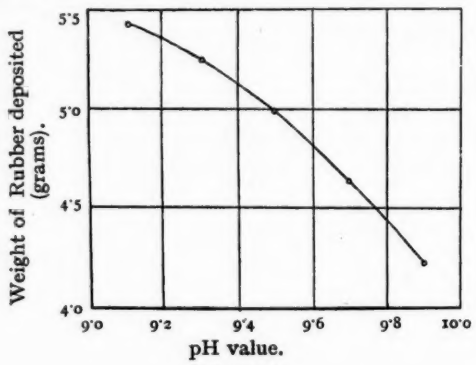


Figure 7

of 0.1 *N* HCl and 0.1 *N* NaOH. The results are given in Tables IV and V and Figs. 6 and 7.

TABLE IV

EFFECT ON THE RATE OF DEPOSITION OF ADDING ACID TO THE BATH

Volume of 0.1 *N* HCl Included in 500 Cc. of Bath	p_H Value of Bath	Average Weight of Deposit
0	9.1	4.28
30	8.0	4.17
50	7.0	3.98
100	6.0	3.58

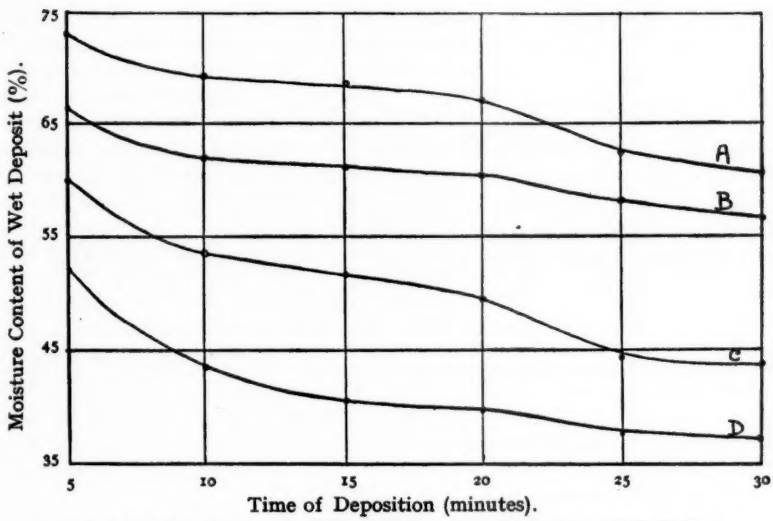
TABLE V

EFFECT ON THE RATE OF DEPOSITION OF ADDING ALKALI TO THE BATH

Volume of 0.1 *N* NaOH Included in 500 Cc. of Bath	p_H Value of Bath	Average Weight of Deposit
0	9.1	5.43
10	9.3	5.24
20	9.5	4.98
35	9.7	4.63
50	9.9	4.22

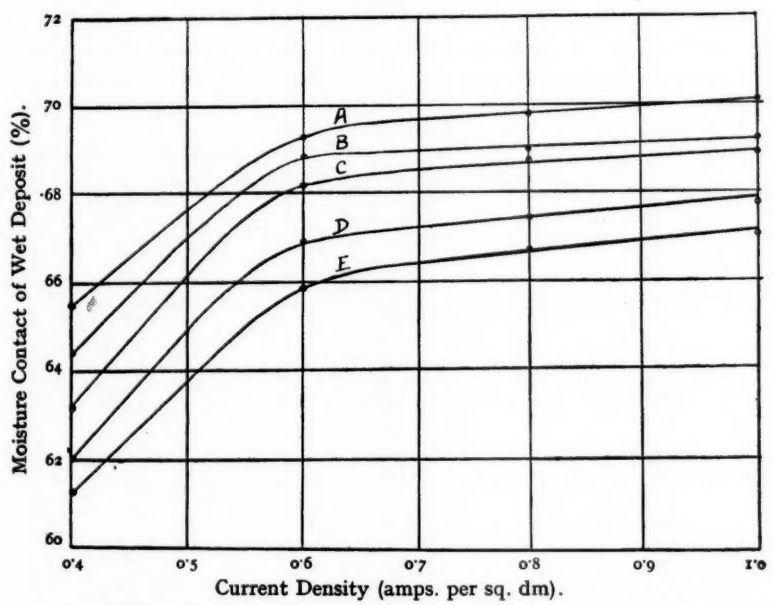
(The above experiments were carried out on two different samples of preserved latex—hence the difference in the weights deposited with no added electrolyte.)

Consideration of the formula for the electrokinetic potential reveals that each of the curves obtained (Figs. 6 and 7) is the resultant of two effects due, respectively,



A 10% D.R.C.; B 15% D.R.C.; C 20% D.R.C.; D 25% D.R.C.

Figure 8



A 10 minutes; B 15 minutes; C 20 minutes; D 25 minutes; E 30 minutes.

Figure 9

to the change in p_H value and the accompanying change in conductivity caused by the addition of acid or alkali. In the former case the change in conductivity will not be great, since the acid is being added to an alkaline medium, and the conductivity of the salt produced will not differ much from that of the original

alkali. Fig. 6, therefore, is probably a fair approximation to the relationship between the p_H value of the dispersion and the rate of deposition within the zone of p_H 6.0 to 9.1. The additions of alkali to an already alkaline dispersion will, however, effect considerable increase in the total conductivity; since the electrokinetic potential is, according to Ghosh and Stamberger (*loc. cit.*), increased by adding alkali, it is very likely from the sharp drop observed in the rate of deposition as the p_H increases from 9.1 to 9.9 that a curve really representative of the change in rate of deposition with increase in the p_H value of the dispersion would tend to a constant maximum value between p_H values 9.0 and 10.0. According to the results of Ghosh and Stamberger, the curve of the electrokinetic potential against concentration of added alkali does flatten out.

Factors Affecting the Nature of the Wet Deposit

Drying conditions exert considerable influence on the appearance of the finished product, and it is essential that the nature of the wet deposit should be such that it will react favorably to drying conditions. The moisture content of the wet deposit is therefore of paramount importance in the technical operation of the process, and it is necessary to control its quantity within relatively narrow limits in order to avoid harmful secondary changes during drying.

1. *The Influence of the Concentration of Rubber in the Bath.*—As the rubber content of the bath increases the moisture content of the wet deposit decreases. This is in agreement with a statement made by Sheppard (*loc. cit.*). The results are shown in Table VI and Fig. 8.

2. *The Influence of the Time of Deposition.*—It is necessary to consider the conditions that arise at the anode; there electrophoresis changes to electro-osmosis.

TABLE VI

THE EFFECT OF CONCENTRATION OF RUBBER AND TIME OF DEPOSITION ON THE MOISTURE CONTENT OF THE WET DEPOSIT

Rubber Concentration (% D. R. C.)	Time of Deposition (Minutes)	Moisture Content (%)
10	5	73.3
	10	69.0
	15	68.5
	20	67.0
	25	62.7
	30	61.1
15	5	66.6
	10	62.0
	15	61.2
	20	60.7
	25	58.4
	30	56.9
20	5	60.0
	10	53.2
	15	51.7
	20	49.5
	25	44.2
	30	43.9
25	5	52.2
	10	43.4
	15	40.3
	20	39.5
	25	37.6
	30	37.0

Either of these phenomena results from the fact that at any surface in contact with a liquid there is an uneven distribution of ions of opposite sign, that is, the surface and the liquid acquire electric charges of opposite sign. Where, as is the case in a dispersion, the surface is free to move, electrophoresis follows the application of an electric field. If, however, the surface is fixed, the application of an electric field to the system causes electro-osmosis and the liquid as a whole migrates toward one of the electrodes.

On reference to Tables VI and VII, Figs. 8 and 9, it will be noticed that the moisture content of the deposit decreases with time. The explanation is that electro-osmosis sets in as soon as a film of rubber becomes deposited upon the anode. Electrophoresis has caused concentration of the rubber in a film at the anode, which is now held in position, and consequently the liquid phase of the dispersion now moves as a whole toward the cathode due to its electrical charge of opposite sign. The film of rubber on the anode is a semi-porous membrane through the pores of which is a constant flow of liquid toward the cathode, and

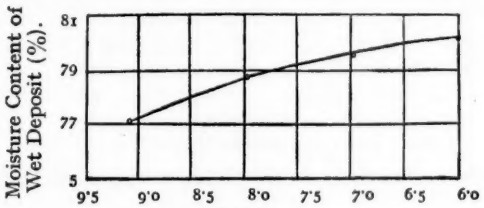


Figure 10

consequently there is a steady fall of moisture content throughout the duration of deposition.

3. *The Influence of the Current Density.*—The moisture content increases with increased current density; results are shown in Table VII and Fig. 9.

TABLE VII

THE EFFECT OF TIME AND CURRENT DENSITY ON THE MOISTURE CONTENT OF THE DEPOSIT

Current Density (Amp./Dm.²)	Duration of Deposition (Minutes)	Moisture Content (%)
0.4	10	65.4
	15	64.4
	20	63.1
	25	62.0
	30	61.2
0.6	10	69.3
	15	68.9
	20	68.2
	25	66.9
	30	65.9
0.8	10	69.9
	15	69.1
	20	68.8
	25	67.5
	30	66.8
1.0	10	70.3
	15	69.4
	20	69.1
	25	68.0
	30	67.2

4. *The Influence of the Nature and Concentration of Added Electrolyte.*—Electrolytes differ widely in their influence on the nature of the wet deposit; in general, an increase in the concentration of added electrolyte gives a softer deposit, *i. e.*, one of higher moisture content, but there are marked exceptions to this rule. Zinc sulfate, with which the present experiments were made, increases the moisture content.

5. *The Influence of the p_H Value of the Dispersion.*—The moisture content increases with decrease in the p_H value of the dispersion; Tables VIII and IX and

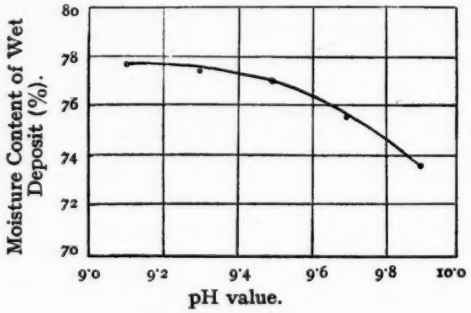


Figure 11

Figs. 10 and 11 give results obtained by adding acid and alkali, respectively, to the bath.

TABLE VIII

THE EFFECT OF LOWERING THE p_H VALUE OF THE DISPERSION ON THE MOISTURE CONTENT OF THE DEPOSIT

Volume of 0.1 *N* HCl Included in 500 Cc. of Bath	p_H Value of Bath	Moisture Content (%)
0	9.1	77.1
30	8.0	78.8
50	7.0	79.7
100	6.0	80.4

TABLE IX

THE EFFECT OF RAISING THE p_H VALUE ON THE MOISTURE CONTENT OF THE WET DEPOSIT

Volume of 0.1 *N* NaOH Included in 500 Cc. of Bath	p_H Value of Bath	Moisture Content (%)
0	9.1	77.7
10	9.3	77.4
20	9.5	77.1
30	9.7	75.6
50	9.9	73.7

Experiments along these lines seem far divorced from factory practice but they do possess considerable practical importance, as only thereby can be determined the relative effects of the different factors influencing the weight of an electrodeposited article and its condition before and after drying. Ideally, manufacture would require to be controlled by physico-chemical determinations, but in practice weight is not restricted to very narrow limits and the operator soon acquires skill in forecasting from their appearance how wet deposits will dry.

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Crystallized Rubber

R. Pummerer and G. von Susich

ERLANGEN AND LUDWIGSHAFEN AM RHEIN

In recent years various attempts have been made to crystallize natural rubber by some means other than by stretching. In the present paper the results of these experiments are described, together with some new observations, in order to settle the present status of the problem.

The processes of crystallization are divided into three groups and discussed individually.

1. Spontaneous crystallization under conditions which vary but little from the normal conditions.
2. Crystallization from solution after purification.
3. Crystallization of a solution of purified rubber by cooling to a low temperature.

1

It is a generally known fact that after storage for a year, plantation rubber becomes stiff, inelastic, and opaque. A rubber altered in this way is known as "frozen" rubber, because this change has been observed most frequently after storage in a cold place. The x-ray investigations of Katz and Bing[1] have rendered it certain that during "freezing" there is crystallization of the rubber, because when subjected to x-rays frozen rubber shows crystalline interferences from which the same crystal lattice is calculated as that which is formed on stretching, except that the degree of orientation in frozen rubber differs from that of stretched rubber. This is seen in x-ray diagrams, where the nearly point interferences of the stretched samples lie on the same Debye-Scherrer circles as those of frozen rubber. There have been rather exhaustive investigations on those changes in frozen rubber which appear on warming, *viz.*, during transformation of the crystalline to the amorphous state (the "fusion process"),[2] and which are characterized by disappearance of the crystal interferences and by a discontinuous change in the heat content, specific gravity, hardness, and light absorption.

Hardly anything is known about the precise conditions of the freezing of rubber. The latter cannot be crystallized in a short time solely by cooling, for after eight days at about −190° C. in the unstretched condition, various samples of rubber, including smoked sheet and films from latex, showed only amorphous diagrams. Moreover, mildly racked rubber shows on cooling to about −190° C. no crystal interferences,[3] for the very intense point interferences observed many times in these roentgenographs come not from rubber crystals but from ice crystals.

In this connection attention should be called to a recent observation of Ott[4] that under the influence of x-rays crepe rubber becomes stiff and opaque, and gives crystal interferences in the unstretched condition. The authors have never observed a stiffening or a crystallization of rubber treated with x-rays, and since little is yet known about the conditions under which crystallization takes place, it remains an open question to what extent in the experiments of Ott crystallization was brought about by x-rays and to what extent by other factors.

When twenty different types of crepe rubber, which were more or less elastic and had none of the characteristics of frozen smoked sheet, were subjected to x-rays, al-

most all appeared crystalline, even in the unstretched condition. Spontaneous crystallization takes place therefore much more easily in crepes than in smoked sheets, which may be attributed to the higher degree of purity of the crepe samples.

2

In 1924 Pummerer and Koch[5] described a method of purification by which certain of the components of rubber most difficult to precipitate separate in crystalline form from the final mother liquor. By means of this procedure, highly masticated smoked sheet was dissolved in benzene, precipitated with alcohol, extracted with acetone in a Soxhlet, again dissolved in benzene, and precipitated by a mixture of benzene and alcohol. The extraction, solution, and precipitation were repeated. After a few weeks it was observed that a yellowish white solid had separated from the benzene-alcohol mother liquor, the quantity of which solid represented several per cent of the original rubber. When purified by recrystallization from ether, it was white, slightly elastic, readily soluble in benzene, and soluble in warm ether. At 60° C. it became transparent and plastic, and around 92° C. it melted completely. Elementary analysis gave the empirical formula $(C_5H_8)_x$. Evaporation of a benzene solution on a watch glass left microscopic double refractive spherolites. According to the investigation of Gross,[6] this substance gave an x-ray diagram which was different from that obtained later with rubber.[7] It was regarded as a crystalline form of rubber.

A short time ago we noticed that the published x-ray diagram[8] of crystallized rubber showed a great similarity to the diagram of the α-modification of gutta-percha hydrocarbon.[9] Moreover, the values given by Gross agreed in the case of the interferences which could be measured exactly with those of α-gutta-percha, and we were able finally to prove that the original diagrams agreed completely with the diagrams of α-gutta-percha. Further confirmation that gutta-percha is present in crystallized rubber was found also in the fact that the solubility obtained by Pummerer and Koch, as well as the softening point[10] and the microscopic structure[11] of the crystallized rubber which has separated from benzene, are exactly like those of gutta-percha.

Finally we subjected an old sample of crystallized rubber to x-rays and obtained its x-ray diagram, together with those of purified gutta-percha. The crystallized rubber at ordinary temperature gave a Debye-Scherrer diagram which was identical with that of α-gutta-percha. When the substance was heated to 70° during the irradiation, it gave only an amorphous diagram, but after cooling the Debye-Scherrer diagram of β-gutta-percha was obtained. The x-ray diagrams of the two samples differ in that the crystalline interferences after heating are not so distinct with crystallized rubber as with purified gutta-percha, because the crystallized rubber after seven years contains considerable amorphous material (probably oxidation products). This is also evident from the fact that, when cooled, the heated samples required a noticeably longer time for crystallization than does pure gutta-percha. This polymorphic transformation of the gutta-percha hydrocarbon on heating, which was proved by x-rays, is so characteristic that there can no longer be any doubt that crystallized rubber is identical with the α-modification.

In answer to the question how a gutta-percha hydrocarbon was obtained as a final product from plantation rubber by the Pummerer and Koch process, we should call attention to the following possibilities:

(*a*) The rubber hydrocarbon has been transformed into the gutta-percha hydrocarbon.[12]

(*b*) At the start plantation rubber contained gutta-percha or balata.

(*c*) The admixture of these substances resulted inadvertently during the long purification.

We consider case (*a*) out of the question, since in the Pummerer and Koch procedure rubber is dissolved, precipitated, and extracted solely under conditions in which a transformation is improbable, and moreover was never observed. As evidence against this transformation, there is also the impossibility of increasing the yield, besides the difficulty of again obtaining crystallized rubber, *i. e.*, gutta-percha hydrocarbon, by the Pummerer and Koch process. We are therefore obliged to decide between cases (*b*) and (*c*).

One of us (Pummerer) has carried out repeated experiments, both with Nielsen and with Pyl and Staerk, in order to obtain larger quantities of crystallized rubber, and there were observed occasionally in the case of the original smoked sheet a few flat spherolites on the walls; however, spherically formed spherolites which could be isolated were never found.

In a sample of smoked sheet of the same origin examined after two years, the various crystalline forms characterized by Gross and found in the chief precipitate KI (cf. Pummerer and Koch, *loc. cit.*) were no longer found. Perhaps the original plantation rubber contained gutta-percha and balata, although it is not known whether these substances are occasionally present in rubber latex. An inadvertent admixture of gutta-percha and balata during the process of purification scarcely enters into the question; this possibility was examined as early as 1924 and was disproved. Consequently, the contamination would have to take place during mastication or at the beginning of the purification process, since the procedure up to the point of the chief precipitation KI is very short, and the older smoked sheets no longer showed crystalline particles in the chief precipitate.

3

Pummerer and Andriessen[13] observed that upon cooling to about $-70°$ sol rubber precipitated almost completely from a one per cent ether solution. When the sample was then cautiously heated to about $-40°$, the greater part liquefied and thin fibers radiating from a point could be seen in the liquid with the naked eye. These maintained their form, but on further heating they dissolved. A similar observation was recently made by Smith.[14] By cooling to $-80°$ an ether solution of highly purified rubber, he obtained fine platelets which again fused together at a somewhat higher temperature. The Bureau of Standards[15] has succeeded, by cooling an ether solution to $-80°$, in obtaining a few rubber crystals and in distilling these *in vacuo* at 100°. We subjected to x-rays at $-70°$ a one per cent solution of sol rubber in a low temperature x-ray chamber. Here the liquid was completely solidified, and therefore no crystalline interferences were obtained. Accordingly, even if they are fibrous, these solid precipitates are not rubber crystals, but only solidified rubber-ether gels, like those obtained by cooling concentrated gelatin solutions. It should be mentioned in regard to the American experiments that one is justified in being sceptical of such results, especially since up to now there have been only very brief reports. As long as nothing more exact (optical behavior, x-ray diagram, melting point, etc.) about these rubber crystals is known, their existence cannot be regarded as free from question.

We have based our opinion on whether a rubber preparation is crystalline, first of all on the x-ray results, which show in a most distinct way whether a substance is crystalline and the type of crystal lattice. Since the crystal lattices of rubber and of both forms of gutta-percha are known sufficiently well, we have in x-rays a means of identifying these subjects and also newly appearing crystalline forms as such.

We must call attention once more to the fact that it has not yet been possible to crystallize rubber from a solution on cooling to low temperature, and to the fact that crystallized rubber is present only in stretched rubber,[16] in frozen rubber,[17] and in most types of crepe.

We wish at this time to show our appreciation to Professor K. H. Meyer for his constant interest and encouragement of this work, and also to Professor Gross for the use of his original x-ray photographs.

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[3] Hengstenberg and Mark, *Z. Krist.*, **69**, 271 (1928); Meyer and Mark, "Der Aufbau der Hoch polymeren Organischen Naturstoffe," Leipzig, **1930**, page 196 and Fig. 74.

[4] Ott, *J. Am. Chem. Soc.*, **52**, 4612 (1930).

[5] Pummerer and Koch, *Ann.*, **438**, 294 (1924); Memmler, "Handbuch der Kautschukwissenschaft," Leipzig, **1930**, pages 193, 514.

[6] Gross, *Ann.*, **438**, 311 (1924).

[7] Katz, *Naturwissenschaften*, **13**, 710 (1925); *Chem.-Ztg.*, **49**, 353 (1925).

[8] Katz, *Ergebnisse der exakten Naturwissenschaften*, **4**, 154 (1925), Fig. 6.

[9] Hopff and von Susich, *Kautschuk*, **6**, 234 (1930). Since the hydrocarbons of balata and gutta-percha give the same x-ray diagram, the latter does not reveal whether a hydrocarbon in question is from balata or gutta-percha.

[10] Kirchhof, *Kautschuk*, **5**, 175 (1929), Table III.

[11] Pummerer and Koch, *loc. cit.* (Diagram 7); Kirchhof, *loc. cit.* (Diagrams 9, 10, 11). Pummerer and Koch give at least three types of crystals in six different structural forms. The various crystal forms of gutta-percha have been described by Kirchhof (*loc. cit.*). de Jong (cf. *Rec. trav. chim.*, **49**, 827 (1930)) has recently shown the existence of three forms which differ in their solubility in benzene. X-rays distinguish only two modifications of the gutta-percha hydrocarbon.

[12] Meyer and Mark, "Der Aufbau der Hochmolekularen Organischen Naturstoffe," Leipzig, **1930**, page 205.

[13] Pummerer, *Kautschuk*, **5**, 133 (1929).

[14] Wolff, *Rubber Age*, **28**, 79 (1930).

[15] *Chem.-Ztg.*, **55**, 63 (1931); *Kautschuk*, **7**, 97 (1931); *J. Franklin Inst.*, **210**, 509 (1930).

[16] Katz, *Naturwissenschaften*, **13**, 710 (1925); *Chem.-Ztg.*, **49**, 353 (1925).

[17] Katz and Bing, *loc. cit.*

[Translated from Kautschuk, Vol. 7, pages 198–202, 217–219, November and December, 1931.]

The State of Rubber in Solutions, Based on the Surface Properties of the Solutions

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The problem of the constitution of rubber and especially of its state in solutions has recently again become the subject of active discussion. Based on a series of investigations, Staudinger[1] reached the conclusion that dilute solutions contain free colloidal rubber molecules which are composed of closed chains of an unusually large number of isoprene residues. Pummerer[2] considers the molecular weight of rubber to be much less than does Staudinger. (According to Staudinger the molecular weight of rubber is 50,000 to 170,000; according to Pummerer it is 1200 to 1600.) Meyer and Mark[3] assume for the primary valence chain of rubber a molecular weight of about 5000. These latter investigators are of the opinion that there are secondary aggregates of rubber molecules in a rubber solution and that the high values which were found by a number of investigators (Caspari,[4] Kroepelin,[5] and others) do not represent the molecular weight but the average micellar weight of rubber. In deciding the question of the state of rubber in solution the majority of investigators make use of the classic cryoscopic and osmotic methods of investigation. Staudinger has used viscosimetric measurements in an original way in his experiments.

In the present work we have turned to a study of the surface properties of rubber solutions, assuming that data along this line might explain some peculiarities in the structure of these solutions.

In fact, if the rubber molecule is composed of a chain of isoprene residues, it must possess a special kind of polarity; hydrophobic methyl groups are opposed to the free hydrophilic double bonds. A molecule of this kind will, according to the views of Harkins and Langmuir, be so located on the boundary surface of a water-benzene solution that the double bonds will be oriented toward the surface of the water and the methyl groups toward the benzene. Such an adsorption must result in a depression of the surface tension (σ) benzene-water. This depression conforms to the well-known formula of Gibbs which is expressed in the following form for weak solutions:

$$\frac{-d\sigma}{dc} = \frac{1}{c} RT\alpha$$

where c is the concentration of the substance in the solution, and α its adsorption in gram moles per sq. cm. of the adsorption surface. According to Langmuir's theory the adsorption reaches a maximum α at definite magnitudes of c when the total surface is occupied by oriented molecules. A monomolecular layer is then formed on the surface which represents, as it were, a crystal of two dimensions. In this case the surface occupied by the adsorbed molecule can be determined by simple calculations, as well as the thickness of the adsorbed layer, in other words, one of the linear dimensions of the molecule. Naturally, any conclusions with regard to the structure of the adsorbed substance must be based on such calculations.

Shacklock[6] has recently studied the surface properties of rubber solutions by measuring the surface tension of the boundary: gas phase/3 per cent rubber solution. The rubber solution was prepared from rubber treated in various ways (masticated, subjected to ultra-violet radiation, etc.). In spite of the precision of this measurement, the data of Shacklock have in our opinion the following fundamental defects. They are concerned with rubber which was not freed from capillary-active impurities, and, moreover, the values of the surface tension, which were determined only for one concentration point, do not permit any general conclusions whatever on the structure of rubber.

I. Discussion of the Method

Pale crepe was used as the starting material for these experiments. Though representing the purest rubber product available, it contains up to 4 per cent of non-rubber components, including proteins, fatty acids, saponifiable resins, sugars, lecithin, etc. Before commencing the experiments it was necessary to obtain the purest material possible, in any case one free from capillary-active substances whose presence would mask the true behavior of the rubber.

For this purpose use was made of a method developed by one of us[7] for the preparation of pure rubber. Finely divided pale crepe was washed several times with a 2 per cent ammonia solution. In this way the rubber is freed from outside impurities, and is also partly freed from non-rubber components which are soluble in alkalies. Their diffusion into the ammonia solution is considerable, since by evaporation of the last fraction of the wash liquor an appreciable residue of fat-like substances remains behind (fatty acid and lecithin (?)). The rubber is then carefully washed free of ammonia and dried in a stream of "absolutely pure" carbon dioxide. Enough dried rubber is put into benzene saturated with carbon dioxide so that a 1 to 1.5 per cent solution is obtained. Solution can be accomplished with simple agitation within 7 to 10 days. A copious precipitate is deposited at the bottom of the vessel, from which the solution is decanted. It is then vigorously agitated in the separatory funnel with one-half its volume of 5 per cent aqueous alkali solution. This forms an emulsion which soon separates into 3 layers, an upper layer, the rubber solution, a lower layer, the aqueous solution, and a middle layer, the emulsion of water in the solution which does not coalesce.

The lower two layers are removed, and the emulsion process is repeated with the alkali solution with the top layer. It is then washed with distilled water until the alkaline reaction disappears. Such treatment doubtless removes from the crepe rubber the capillary-active non-rubber components which, because of adsorption, have concentrated chiefly in the middle layer which is poured off. Finally, the rubber is precipitated with acetone from the upper layer and the precipitate is again extracted for 12 hours with acetone in the Rodemacher apparatus. The product obtained by such treatment contains no nitrogen, as judged by a Kjeldahl microanalysis. It is further fractionally precipitated from the benzene solution by Pummerer's method.[8] The easily soluble fraction is used in these experiments. The rubber is freed from the solvent and especially from the acetone by drying at 30°–50° C. in a current of carbon dioxide, which is led over a copper screen through the electric oven (for the purpose of removing the oxygen which might be contained in the carbon dioxide). As a result of all of these operations, a transparent product is obtained which is easily soluble in benzene without any residue. This rubber product is designated by the index K_1 in the following discussion.

It should be mentioned that in order to prevent oxidation of the rubber, all operations after the alkali purification must be carried out in an atmosphere of

carbon dioxide and, in fact, with solvents saturated with carbon dioxide (oxygen-free).

A further series of measurements was carried out with a product which had been prepared as follows: The easily soluble rubber fraction, obtained by the process described above, was dissolved in benzene and again emulsified with a large quantity of water. On standing, the system separated into two layers (see Fig. 1), of which the lower one gave a very stable emulsion (perhaps water in rubber-solution). The upper layer, *i. e.*, the rubber solution, was transferred in a Wurz flask filled with carbon dioxide connected with a vacuum pump. The solvent was distilled off at room temperature. The rubber remained as a completely transparent adherent film on the walls of the flask. The flask was again filled with carbon dioxide and the rubber it contained was dissolved for the subsequent experiments. This product is designated by the Index K_2.

Figure 1

The surface tension was measured in our experiments at a temperature of 20° C. with the Rehbinder[9] apparatus, which is constructed according to the Cantor principle of the determination of σ from the maximum pressure of small bubbles. Our experiments with the Donnan pipette have shown that in many cases this gives results which are not consistent and are therefore contradictory. This latter fact was proved by qualitative experiments on the stability of aqueous emulsions of rubber solutions of different concentrations. In a complete series of emulsions the most stable was that which gave the highest surface tension by the Donnan method and the lowest by the Rehbinder method. This fact shows plainly that the latter method is to be preferred.

In some experiments the Rehbinder apparatus was connected with a V-tube which was filled with glass wool wet with benzene in order to protect the rubber solution against the action of atmospheric oxygen. This tube was connected with a tall cylinder (*a*) filled with carbon dioxide. The apparatus is shown in Fig. 2. Before beginning the experiment, the beaker (*b*) and the pipette were filled with carbon dioxide by means of a suction apparatus (*c*), and not until then were measurements of the surface tension made. It should be mentioned, however, that within the time required to carry out an experiment, atmospheric oxygen showed no noticeable influence on the σ of the rubber solution. Measurements taken at intervals of 30–40 minutes gave consistent results. In this way the precautions mentioned were of no real importance.

II. Surface Tension at the Boundary Surface of a Water-Benzene Solution

The surface tension at the boundary surface of a water-benzene solution shows characteristic changes which depend upon the concentration. At low concentrations the σ of the rubber solution is less than that of the pure solvent. This difference becomes still greater with increasing rubber content in the solution, and it reaches a minimum between 0.5 and 0.7 per cent. Furthermore, an increase

in σ was observed, and at a content of 1.5 per cent a maximum surface tension was reached, which exceeds the σ value of the pure solvent. In other words, at the boundary water solution, rubber behaves in low concentrations like a capillary-active substance, whereas in concentrations above 0.7 per cent it behaves like a capillary inactive substance.

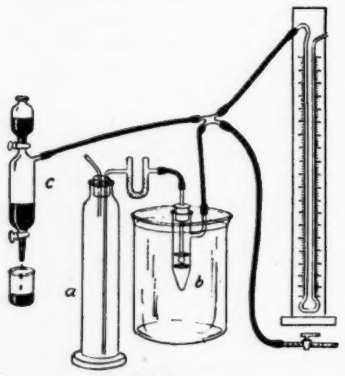


Figure 2

The character of the isotherm (σ, c) depends to a great extent on the purity of the preparation. The solution of unpurified rubber shows a sudden decrease in the surface tension with concentration, which is very characteristic of capillary-active substances. The minimum was at 0.7 per cent and at σ is 17.75 ergs per sq. cm. The minimum values of σ increased in proportion to the purity of the rubber and finally attained a more or less constant value. Preparation K_2 had a surface tension of 30.83 ergs per sq. cm. at the minimum (0.5 per cent). The maximum σ value was 34.19 ergs per sq. cm. for a 1.38 per cent solution. The results of the individual measurements are given in Table I and Fig. 3.

TABLE I

SURFACE TENSION AT THE BOUNDARY WATER-SOLUTION OF DIFFERENT SAMPLES OF RUBBER AT 20°

σ_0 Water-Benzene = 32.3 Ergs per Sq. Cm.

Concentration in %	Unpurified Pale Crepe in Ergs per Sq. Cm.	Rubber K_1 but without Acetone-Extract, Ergs per Sq. Cm.	Rubber K_1 in Ergs per Sq. Cm.	Rubber K_1 in Ergs per Sq. Cm.	Rubber K_2 in Ergs per Sq. Cm.
0.125	30.12	32.33	30.96	31.81	31.87
0.250	26.44	33.06	30.96	31.74	30.92
0.500	19.84	31.69	33.06	31.37	30.83
0.700	17.75	28.67	32.33	32.26	33.10
1.000	22.06	30.86	33.06	32.24	34.16
1.38	...	...	...	...	34.19
1.5	...	30.03	33.80	33.21	...
2.0	...	30.03	35.27	33.36	...

A minimum in the isotherm of the surface tension of rubber is an anomaly, in contrast to the typical isotherms of capillary-active substances. However, in this respect our results are similar to those of du Nouy[10] for blood serum and oleic acid, and are therefore similar to the measurements of the surface tension of latex.[11] This minimum can be explained from two points of view. Granted that the special character of the isotherm (σ, c) is dependent only on the influence of foreign capillary-active substances, then the origin of this minimum lies in the kinetic behavior during the formation of the adsorption layer and in the peculiarities of the methods used to measure the surface tension. As is known, the value of σ was determined according to the method of Cantor in each individual case. This value corresponds to the adsorption membrane, which forms on the surface of the drops at the moment of leaving the pipette. To obtain a "static" value for σ an extraordinarily slow formation of the drop is necessary, so slow in fact that in the time interval of its growth an adsorption layer can form and come to equilibrium. In viscous liquids,

in which the diffusion is difficult, it may happen that the time of the formation of the drop is insufficient for the complete formation of an adsorption layer. The experimental value for σ would then be different from those values which actually correspond to the adsorption equilibrium. In our case, we have such a liquid. It can be assumed that in dilute rubber solutions, up to 0.5 per cent, diffusion is more or less unhampered and that the foreign capillary-active substances present restrict the usual change in surface tension with change in concentration, which corresponds to the descending part of the isotherm (Fig. 3). With increase in concentration, the diffusion of these substances becomes more and more difficult, and the values found for σ become greater than corresponds to their content in the solution. The greater the viscosity of the solution, *i. e.*, the greater their concentration, the greater is this difference. For this reason there can be an ascending part of the isotherm after a minimum.

This sort of an explanation of the results can, however, in a way apply only to the isotherm of the solution of unpurified pale crepe (Fig. 3, curve 1). For solutions of purified rubber, *i. e.*, preparations K_1 and K_2, it has been proved untenable. In fact, the very nature of the methods used by us for the purification of rubber makes it possible to count upon the removal of capillary-active substances. That the purification of rubber is brought to the utmost extent is evident from the fact that preparation K_2 had a lower minimum surface tension than did preparation K_1 which was purified by a simpler method. In order, however, to be convinced that the character of the isotherm (σ, c) depends not only on the kinetic behavior during the formation of the adsorption layer and not upon the calculation of the non-rubber components in the solutions under investigation, the following experiment was carried out. A 1.5 per cent solution of preparation K_1 was exposed in an atmosphere of carbon dioxide to the radiation of a quartz lamp up to the point where the viscosity reached the same value as that of a 1 per cent solution which had not been exposed. The surface tension of this solution was measured at the concentrations at which the values of the relative viscosity corresponded to the measured points of the unexposed solution of preparation K_1. The surface tension of the exposed rubber differed sharply from that of the original products (a second communication will deal with this). If the values of the surface tension are plotted as ordinate and the corresponding viscosity values η as abscissa in a system of coördinates, a comparison of the curves shows that they are wholly independent of one another (Fig. 4). If the character of the isotherm (σ, c) were determined only by the kinetic relations of the adsorption of non-rubber components, which

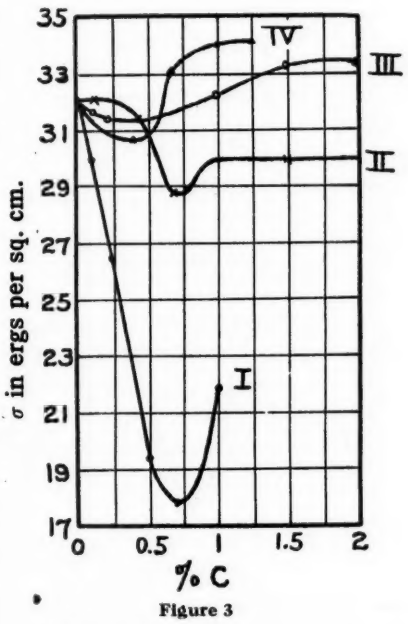


Figure 3

I—Pale crepe unpurified
II—Rubber K_1 without acetone extract
III—Rubber K_1 IV—Rubber K_2

among other things depend upon the viscosity of the solutions, then both curves would have several points in common, which is not the case.

Attention should be called to the fact that the ascending part of the isotherm of purified rubber (preparations K_1 and K_2) extends beyond the value of the surface tension of the pure solvent. These facts can in no case be explained by the influence of non-rubber components in the solution which resemble capillary-active substances. In contrast to earlier expressed opinions we are inclined to the view that the peculiarities of the isotherm of the surface tensions of solutions of pure rubber depend on the properties of rubber itself, and are related to changes in its structure. In agreement with Staudinger,[12] we assume that in dilute solutions chain molecules of rubber are present, which have a peculiar kind of polarity, as we have already mentioned earlier. As a result of the existence of free double

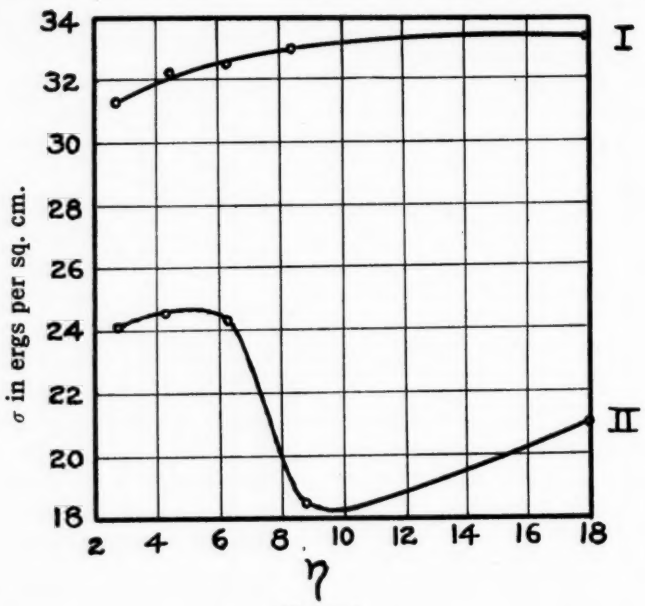
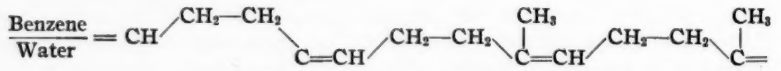


Figure 4
I—Rubber K_1 not irradiated II—Rubber K_2, irradiated

bonds and of methyl groups, these molecules are oriented in the surface layer of water-benzene and decrease its surface tension. On the assumption that the molecular chain of rubber is so located that its methyl groups point toward the benzene surface and the double bonds toward the water surface, this oriented arrangement of the molecules on the boundary surface of benzene-water can be represented in the following way:



Consequently, in dilute solutions rubber behaves like a capillary-active substance. In concentrated solutions, however, the rubber molecules are aggregated into complexes of the second order, as a result of which this aggregation is accompanied by a closing of the double bonds. The rubber micelles formed have a

sharply hydrophobic character, which is manifest also in the increase in the surface tension of the solution. This phenomenon corresponds to the ascending part of the isotherm. The hydrophobic character of the rubber micelles is apparently related to the presence of free methyl groups on their surface. This hydrophobic nature of rubber is fully manifest in 1–1.5 per cent solutions, in which the surface tension reaches its highest value.

An explanation of the anomalous isotherm of the surface tension of rubber is verified by the following facts. On the one hand, Staudinger[13] has pointed out that the aggregation of the rubber molecule with increase in concentration of solutions leads to deviations from Einstein's law of viscosity. According to our measurements (Fig. 5), this deviation in pure rubber solutions is within the limits of 0.4 to 0.6 per cent. The deviation from the Hagen-Poiseuille law[14] for these solutions falls within exactly the same limits, as shown in Fig. 6 and Table II. It is therefore evident that the limits of concentration of the transition from the molecular to the micellar state, which we have found by the isotherms of the surface tension of rubber solutions, correspond to the same limits as those calculated from viscosimetric data.

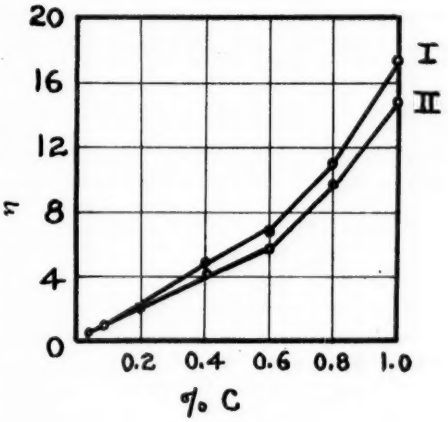


Figure 5

TABLE II

VISCOSITY OF SOLUTIONS OF PREPARATION K_1 AT DIFFERENT PRESSURES OF FLOW

Pressure P in Cm. Water Column	C 1%	C 0.8%	C 0.6%	C 0.4%	C 0.2%	C 0.1%	C 0.05%
10.5	17.71	11.31	7.14	5.42	2.38	1.46	1.18
20.5	15.41	9.92	6.55	4.57	2.27	1.57	1.18
40.5	14.03	9.68	6.22	4.48	2.08	1.41	1.17
60.5	13.47	6.61	5.61	4.24	2.07	1.37	1.18

III. The Adsorption of Rubber at the Boundary Surface: Water/Benzene. Structure of the Adsorption Layer

With the aid of the values of the isotherms of the surface tension, the adsorption of rubber at the boundary surface: water/benzene solution, can be calculated by the Gibbs equation. It is, of course, understood that this calculation is applicable only to the descending part of the isotherm. Table III gives the values for K_1 and K_2.

TABLE III

ADSORPTION OF RUBBER IN MOLS PER SQ. CM.

$$\alpha = \frac{1}{RT} C \frac{\Delta\sigma}{\Delta C}$$

C in Mols per Liter	Rubber K_2
0.0092	1.50×10^{-11}
0.0276	2.77×10^{-11}
0.0368	2.85×10^{-11}
0.0551	5.54×10^{-12}

When these values are plotted, they do not conform to the Langmuir equation. Nevertheless, the values were used in a rather arbitrary way to calculate the surface on a hydrophilic group at the maximum adsorption (maximum α) which, according to the concept of the authors, means on a double bond of the isoprene nucleus.

As is evident from the table, the maximum adsorption, calculated by the Gibbs equation, for K_2 is 2.85×10^{-11} mols per sq. cm.

The Gibbs equation has the form: $\alpha = -\frac{1}{RT} \cdot \frac{\Delta\sigma}{\Delta C}$, where C is the concentration of the substance in gram-mols. C is determined by the ratio $\frac{a}{M}$, where a is the weight of the substance in grams per liter, and M is the molecular weight. From this it is easily seen that the extent of the adsorption, expressed in gram-mols per sq. cm., does not depend upon any particular molecular weight chosen for the calculation. An M value of 68 is assumed, and this was used in the further calculations of the isoprene nuclei of the rubber molecule. On the assumption that at the maximum adsorption (maximum α) the surface layer is completely occupied by oriented rubber molecules, the surface pertaining to a hydrophilic group can be calculated according to the concept of Langmuir and Harkins, *i. e.*, by the equation: $S = \frac{1}{(\text{max. } \alpha)N}$ where N is the Avogadro number.

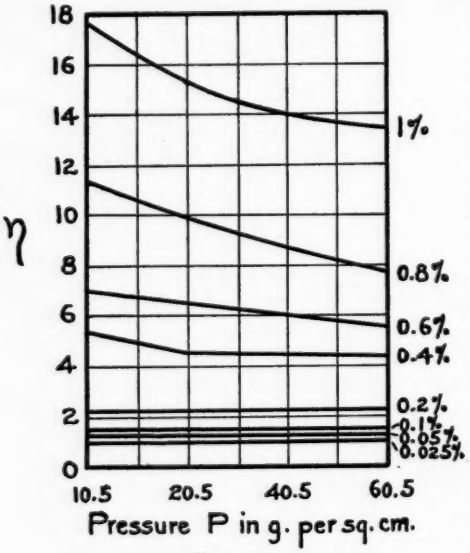


Figure 6

In the present case the values of K_2 lead to an S value of 60×10^{-15} sq. cm. Based on measurements of the surface tension of oleic acid, Lecomte de Nouy[15] calculated the surface S occupied by one double bond to be approximately 50×10^{-16} sq. cm.

According to the measurements in the present work, there is in the thickest adsorption layer of rubber almost twelve times as great a surface on a double bond as the value calculated for a regularly formed monomolecular layer of oleic acid.

This leads to the conclusion that rubber does not form at the boundary surface: water-benzene, a monomolecular layer with the properties of crystals of two dimensions. An orientation of the rubber molecules in close parallel rows is necessary for this structure, and such an orientation is made difficult by the unusual length of the molecular chains of rubber. In the present case, it is well to mention that Locher and Stiebel[16] did not succeed in obtaining rubber films with the properties of crystals.

On the other hand, the calculations in the present work do not conform to the data of du Nouy (*loc. cit.*), which indicate that the union of rubber molecules to micelles of the second order takes place before the attainment of the adsorption equilibrium which corresponds to the thick monomolecular film. This union to

micelles does not take place suddenly at a definite limiting concentration, for even in dilute rubber solutions it is possible for aggregates of the second order to coexist with rubber molecules. Their presence makes difficult the formation of a thick monomolecular film.

On the basis of the discussion above, the limiting concentration of the transition of rubber from the molecular to the micellar state, which is shown in Part II of the present work, must be regarded as the limit of its transition from the predominantly molecular to the predominantly micellar state.

IV. Surface Tension at the Boundary Surface: Gas Phase (Air)/Benzene

The surface tension of rubber at the boundary surface of the gas phase was measured with the same Rehbinder apparatus. In order to prevent the evaporation of solvent from the surface film, air (or carbon dioxide) previously saturated with benzene vapor was forced through the pipette.

As was to be expected, rubber showed itself to be, like other capillary-active substances[17], capillary-inactive at low concentrations at the gas surface, in contrast to the boundary surface: water/benzene, *i. e.*, it increases the surface tension of the pure solvent. The results which indicate this fact are, however, not wholly incontrovertible. For example, measurements of the preparation K_2 at three different concentrations in an atmosphere of carbon dioxide showed a lower surface tension than that of the pure solvent. With increase in the rubber content in the solution, the surface tension diminished until it reached that of the pure solvent.

TABLE IV

SURFACE TENSION AT THE BOUNDARY SURFACE: GAS PHASE/SOLUTION, AT A TEMPERATURE OF 20° C. (IN ERGS PER SQ. CM.)

σ = air/benzene = 29.40 Ergs per Sq. Cm.

C in %	Rubber K_1 without Acetone Extraction, σ	Rubber K_1, σ	Rubber K_2 in Carbon Dioxide, σ
0.125	29.39	29.75	28.65
0.25	29.39	30.19	29.02
0.50	29.39	29.75	29.39
0.70	30.62	29.39	29.39
1.00	29.29	29.39	29.39
1.50	29.39	29.39	29.39
2.00	29.39	30.13	29.39

These results show that, beginning with a concentration of 1 per cent, rubber (unaltered) has no appreciable influence on the surface tension of the pure solvent. The same result was obtained by Shacklock,[18] though the absolute values of his measurements differ somewhat from those of the experiments in the present work. This can be explained by a strong solvation of the rubber micelles, which have a slight polarity and therefore have no appreciable influence on the surface tension of the pure solvent. All this points to a micellar condition of rubber in solutions over 0.7 per cent concentration.

Conclusions

1. To determine the state in which rubber exists in solutions, the surface tension of these solutions at the boundary surface: water/gas phase, was studied.

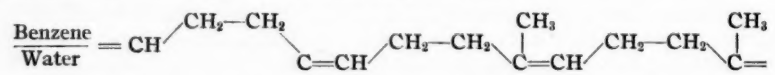
2. Crude rubber contains a considerable quantity of capillary-active substances such as proteins, fatty acids, sugar, lecithin, etc. For this reason, a method of purification of the rubber was used which guaranteed the removal of these sub-

stances. As a rule, all operations were carried out in an atmosphere of carbon dioxide to prevent oxidation of the rubber.

3. At the boundary: water/benzene solution, pure rubber behaved at concentrations up to 0.5 per cent like a capillary-active substance, whereas in concentrations above 0.7 per cent it behaved as a capillary-inactive substance. The isotherm of the surface tension showed a minimum between 0.5 and 0.7 per cent.

4. This behavior of rubber solutions can be explained on the assumption that dilute solutions (in agreement with the views of Staudinger) contain chiefly free colloidal rubber molecules, which contain hydrophilic double bonds. In concentrated solutions there is an aggregation of molecules into large complexes, with union of the double bonds. The hydrophobic methyl groups of the isoprene nuclei remain free.

5. On the assumption that the double bonds of the isoprene nuclei are turned toward the water and the methyl groups toward the benzene solution, the arrangement of the rubber molecules at the boundary surface: benzene/water, can be represented schematically in the following way:



6. The explanation of the character of the isotherm of the surface tension of rubber (see paragraph 4 above) is confirmed by the fact that the viscosity of rubber solutions in concentrations less than 0.5 per cent follows the Einstein and Hagen-Poiseuille laws. In higher concentrations there is a deviation from these laws, which is attributed by many authors to the micellar state of the solutions.

7. The calculation of the adsorption, from the isotherm of the surface tension, gives values which are at variance with the formula of Langmuir. However, subject to reservations, the surface of one isoprene group for the maximum adsorption was calculated to be 60×10^{-15} square centimeters.

8. Since, according to the measurements of du Nouy, the surface occupied by a double bond in a molecular layer is 50×10^{-16}, rubber does not, on account of the unusual length of its molecular chains, form a thick molecular layer with the properties of a 3-dimensional crystal, and the aggregation of rubber molecules to micelles takes place before the formation of the adsorption equilibrium which is essential to the formation of a thick molecular film.

9. At the boundary surface: air/benzene solution, rubber is capillary-inactive in concentrations up to 0.5 per cent, whereas at higher concentrations it has no appreciable influence on the surface tension of the pure solvent. This may be explained by a strong solvation of the rubber micelles.

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Rubber Solutions

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In my earlier publications[1] the hypothesis was suggested that rubber is a homogeneous substance and not a mixture of homologous polymers. This hypothesis has been criticized from many sides. My conclusions were based on the fact that the diminution of the vapor pressure and of the osmotic pressure of rubber solutions is independent of the origin of the rubber and of the treatment it receives.

With regard to the discussion of the objections which have been made,[2] I have obtained evidence that this hypothesis is also supported by other quantitative measurements of the state of equilibrium, *e. g.*, the specific heat.[3]

In the course of this discussion, Bary[4] questioned the basic theory by which I arrived at this conclusion when the incompatibility of the Raoult law has been established.

Figure 1

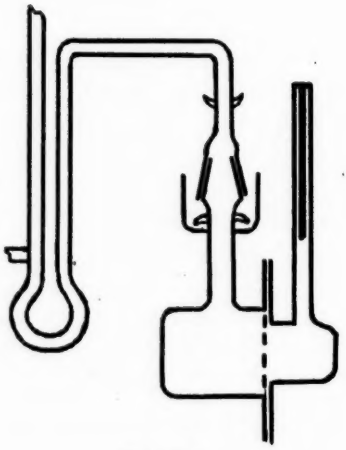

Figure 2

Kroepelin[5] calls attention to the fact that, in concentrated swollen substances, molecular groups and not molecules are united with the solvent. In the case of rubber these have double bonds.

I do not know any reason that can justify this conclusion of Kroepelin. The investigations which I have undertaken on more dilute solutions do not support such a theory. A little later I shall go into more detail about Bary's comment.

The results of the measurements of the osmotic pressure will be given later. Toluene was used as the solvent, and the solutions varied in concentration from 1 to 5 per cent. Figures 1 and 2 show the apparatus which was used. This apparatus contains a membrane which is fastened between the rims. These membranes were prepared from filter paper (Schleicher and Schüll, white band) impregnated with 4 per cent rubber solutions. After impregnation, the membranes were vulcanized with a solution of 1 per cent sulfur chloride in benzene. These

membranes are practically impermeable to rubber. Figure 2 shows the apparatus, which is based on the principle applied also by Buchner and Samwell.[6] If the membrane is permeable, no reproducible result can be obtained. The measurements are reproduced in Fig. 3.

The results do not permit the application of known methods for calculating the molecular weight. At the present time, my views are represented as follows. Sometime ago I showed[7] that the equations:

$$p = \frac{k}{v^2} \quad \text{or} \quad P = kc^2,$$

representing the change in the molecular attraction as a function of the dilution

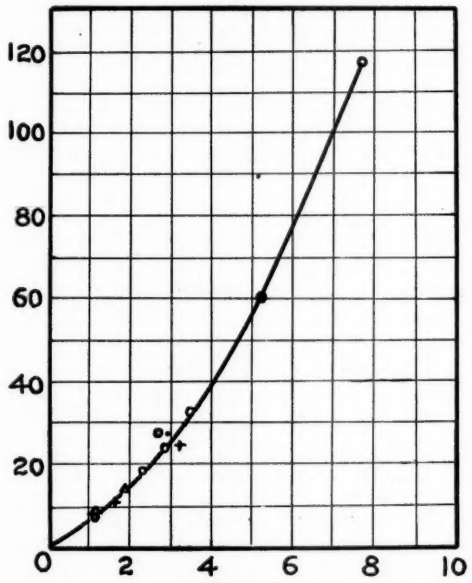

Figure 3

⊙ Sample I (first latex crepe of 1926) masticated
\+ Sample II (first latex crepe of 1929) masticated
⊗ Sample III (first latex crepe of 1929) very highly masticated
• Masticated in absence of oxygen (in nitrogen)
△ Rubber isolated from latex

(or concentration) are applicable also to swelling. Constants k are given in Table I.

This relation was also applied to express the relation between the molecular attraction and absorption by Polanyi and London,[8] in the form:

$$p = \frac{k}{d^6}$$

where d is the distance. In the first case the attraction potential is:

$$A = -kv$$

When $v = 1$, $A = -k$.

The masses of these molecules, which are the centers of attraction, constitute a determinant factor in the evaluation of this attraction potential in agreement

TABLE I

Substance and Solvent	P (Osmotic Pressure in G. per Sq. Cm.)	v (Cu. Cm. Solvent per 1 G. Dissolved Substance)	k
Rubber			
Benzene	853	5.83	29000
	1253	5.	31000
	2253	3.72	31000
	3253	3.09	31000
	5253	2.36	29300
Toluene	116	13.6	21500
	250	11.5	33100
	399	9.2	36800
	654	7.4	35800
	900	6.7	40500
	1720	4.8	39900
	2253	3.9	35300
	5053	2.55	32100
	5053	2.43	31000
Chloroform	163	16.3	43300
	292	13.1	50000
	536	10.15	54600
	605	9.1	50100
	1253	6.2	49300
	2253	4.7	50700
	4253	3.4	49100
	5253	2.88	43600
Carbon tetrachloride	1253	6.9	59500
	2253	5.3	63000
	3253	4.2	57300
	4253	3.7	60100
Gelatin			
Water	653	2.55	4240
	1253	2.06	5300
	2253	1.46	4800
	4253	1.09	5053
	5253	0.92	4494

with our knowledge of the molecular attraction of gases and liquids. The similarity of the curves of the various rubbers indicates that the masses of the dissolved rubber molecules are the same.

This fact supports the concept held by many investigators that rubber is a homogeneous substance.

My osmotic measurements do not lend any support to the idea of Staudinger.[9] There is no relation between the osmotic pressure and the viscosity of these solutions.[10]

To conclude, I must not fail to mention that there are a number of phenomena for which one cannot give a satisfactory explanation at present if we depend upon the concept just mentioned, and for this reason the final word has not been said.

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[2] *Kautschuk*, **6**, 159 (1930).
[3] Ruhemann and Simon, *Z. phys. Chem.*, **138**, 1 (1928).
[4] *Kautschuk*, **6**, 199 (1930).
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Isoprene and Rubber

Part 33. End Groups in Rubber

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In a recent work, Pummerer, Ebermeyer, and Gerlach[1] attempted to identify end members in the rubber molecule by ozone decomposition, and in this way to determine the molecular weight of rubber by chemical means. In this connection they say:

> The basis for the validity of the conclusions derived from the cleavage fragments on the average length of the rubber chain is that this hydrocarbon contains no structurally foreign impurities, but is built up of homogeneous molecules, though of perhaps different lengths.[2]

Pummerer abandons his earlier view, according to which rubber is composed[3] of a uniform base molecule, in favor of concepts held by me for years on the constitution of rubber and other high polymeric substances. As was first proved for synthetic products[4] and as shown for balata[5] and rubber, these substances consist of a mixture of similarly constituted molecules of various lengths and therefore of a mixture of homologous polymers. Pummerer has now adopted this concept, but on the other hand he does not agree on the question of the molecular weight.

It is now possible in many cases to determine the molecular weight of such long fiber molecules by chemical methods, *i. e.*, when these molecules have a characteristic end group and if it is assumed that all molecules in the mixture of homologous polymers of the same kind have the same end groups. This mode of operation was applied for the first time[6] in explaining the constitution of polyoxymethylenes. With rubber on the contrary there is no prospect of success with this method, for such long fiber molecules are present that an end group cannot be determined analytically for certain, since it is too small a part of the molecule. The molecular weight of purified rubber is about 68,000. Accordingly, there are on the average in the rubber molecule about 1000 isoprene residues united to form a long chain.[7] If two terminal isoprene residues have as end groups a somewhat different grouping from the average 1000 internal members, then the isoprene residues cannot be detected by chemical methods like ozone decomposition, because they make up only 0.2 per cent of the total molecule.

The determination of the size of the molecule by chemical methods is possible only in the case of hemi-colloidal molecules (*i. e.*, molecules of an average degree of polymerization of about 100) in case characteristic end groups are present, since in such a case these end groups are a large enough part of the total molecule to be detected analytically.

An average degree of polymerization as small as about 100 is not to be considered for rubber, however, as I have already indicated many times.[8] Polyprenes of this average degree of polymerization have entirely different properties; they show a hemi-colloidal character.[9]

In this latest work Pummerer leaves unsettled the numerous experiments on the structure of high molecular hydrocarbons and especially of rubber, and he utilizes methods of determining the molecular weight which is not applicable in this field.

References

[1] *Ber.*, **64**, 809 (1931).
[2] In this connection see my investigation of these methods (*Kolloid-Z.*, **54**, 132 (1931)).
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[7] Staudinger and Bondy, *Ibid.*, **63**, 734 (1930).
[8] *Ber.*, **59**, 3036 (1926); *Ann.*, **468**, 1 (1929); *Ber.*, **63**, 734, 921, 2888 (1930); *Helvetica chim. Acta*, **13**, 1324, 1361 (1930).
[9] Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[Translated in abridged form from Annalen der Chemie, Vol. 488, No. 2, pages 127–153, July 29, 1931.]

Isoprene and Rubber

Part 34. Molecules or Micelles in a Rubber Solution

H. Staudinger and H. F. Bondy

Measurements of the Viscosity of Rubber Solutions

In the literature may be found numerous measurements of the viscosity of rubber solutions, the object of which was to throw light on the nature of colloidal solutions and changes in these solutions by various operations. These investigations give no insight into the structure of colloid particles and the reason for changes in rubber solutions because they are based on false assumptions, particularly the assumption that rubber has a micellar structure. Often highly viscous solutions were studied, and though these appeared to be of special interest to the colloid chemist, they were unsuited for such investigations, for they are gel solutions in which the structure of the colloid particles is much more difficult to explain than is that in dilute solutions (sol solutions), where the molecules have freedom of movement and do not disturb one another. The earlier works also contain references to the sensitivity of rubber to oxygen, though no special precautions were ever taken in the measurements to exclude oxygen; in fact this was unnecessary as a rule, for crude rubber solutions are much more stable, because of anticatalysts present, than solutions of pure rubber in which these have been removed.

Pure rubber was prepared by the method of Pummerer and Pahl[1] and, as described in the following work, was separated by fractional extraction into portions of different average molecular weights. Viscosity measurements of the individual fractions were then carried out under various conditions.

The study of the rubber solution, like that of the balata solution, must be carried out with complete exclusion of air, and the solvent (tetralin or benzene) must be distilled in an atmosphere of pure nitrogen and be freed of oxygen.[2] The filtration of the rubber solution, the filling of the viscosimeter, as well as the measurements themselves, are likewise made in an atmosphere of pure nitrogen. Measurements were taken in the Ubbelohde viscosimeter at different pressures, as a rule at 10.30 and 60 cm. mercury pressure. Very dilute solutions were also measured in the Ostwald viscosimeter, since the deviations from the Hagen-Poiseuille law are of no great importance at low concentration.

Finally, it should be mentioned that these special precautions during the viscosity measurements, above all the careful exclusion of air, are necessary only in the case of rubber, not with the saturated hydrocarbons, polystyrene, and hydrorubber.

Deviations from the Hagen-Poiseuille Law

Just as Kirchhof[3] proved for the first time, and as has been frequently confirmed since, rubber solutions do not obey the Hagen-Poiseuille law. Accordingly, it does not seem possible to draw any conclusions about the molecular weight from viscosity measurements, since the viscosity itself changes with the constants of the apparatus, *i. e.*, the width of the capillary tube and the pressure by which the solution is forced through the capillary tube. In concentrated solutions, the relative viscosity at low pressures is double that at high pressures. At very high pressures it becomes constant, as was first established by Hess.[4] In agreement with the earlier ideas on the nature of a colloidal rubber solution, these deviations from the

Hagen-Poiseuille law were considered to be related to some form of internal structure. Thus in a recent work Dogadkin and Pewsner[5] have said:

> Wo. Ostwald[6] suggests designating the viscosities of these P values as "structure viscosity." Such a designation must be regarded as well chosen, since the deviation of the colloid at low pressures from the Hagen-Poiseuille law is related to the polyphase internal structure and to changes in the micellar structure of the colloid, which may take place even with insignificant changes in the rate of flow.

It has now been proved in the case of polystyrenes that the longer the molecules the greater are the deviations from the Hagen-Poiseuille law.[7] The same relations were also found by the authors[8] for balata solutions.

These deviations from the Hagen-Poiseuille law were attributed to the fact that the long fiber molecules, which are irregularly arranged in the stationary liquid, become oriented in parallel by the flowing liquid and therefore the current offers less resistance than when they are disordered, a concept which has also been proved by experiments by Signer[9] on the double refraction of a stream of colloidal molecules. Since the abnormal viscosity phenomena of colloidal molecules depend upon the length of the molecule, they are called macromolecular viscosity phenomena in order to distinguish them from the abnormal phenomena of other colloidal solutions, *e. g.*, soap solutions.[10]

TABLE I

0.2-BASE MOLECULAR SOLUTIONS OF RUBBER IN TETRALIN

Molecular Weight 10^{-3}	η_r with Rate of Fall[13] 200	1500	$\frac{\eta_{200}-\eta_{1500}}{\eta_{1500}}\times 100$	η_r 10 cm. Hg	60 cm. Hg	$\frac{\eta_{10}-\eta_{60}}{\eta_{60}}\times 100$
225	22.0	14.5	52	24.2	15.8	53
140	16.6	12.5	33	17.1	13.0	31
110	15.0	11.5	30	15.1	11.7	29
105	14.7	11.1	32	15.0	11.3	33
100	13.9	10.7	30	13.8	10.8	28
100	13.4	10.2	31	13.4	10.2	31
80	12.4	9.6	29	11.5	9.1	26
70	10.6	8.7	22	10.4	8.2	27
60	9.3	7.7	21	9.1	7.6	20
50	6.5	5.7	14	6.3	5.5	15
40	5.0	4.8	4	5.0	4.5	11
40	4.6	4.5	2	4.7	4.3	9
25	3.0	2.9	3	2.9	2.8	4
11	1.79	1.78	0.6	1.78	1.76	1
10	1.68	1.67	0.6	1.67	1.66	0.6

Solutions of rubbers of different average molecular weights were then examined in the Ubbelohde viscosimeter, and in this way the same relations were found as with polystyrene and balata. Solutions of low molecular rubber show only slight macromolecular viscosity phenomena. Not until a molecular weight of 40,000 is reached do these phenomena become more noticeable. In the highest molecular rubbers of molecular weights of 100,000–200,000, the phenomena are pronounced. In all, sixty rubber fractions of average molecular weights of 10,000–225,000 were measured.

The dependence of the Hagen-Poiseuille law can be indicated simply by expressing the difference in the relative viscosities at 60 cm. and 10 cm. excess mercury pressure in per cent: $\frac{\eta_{10}-\eta_{60}}{\eta_{60}}\times 100$.[11]

These values can be utilized for obtaining a tentative estimation of the deviations from the Hagen-Poiseuille law (see column 7 of Table I). To obtain more precise

values the velocity of fall was calculated by means of the Kroepelin equation[12] from the viscosity measurements at various pressures:

$$GF = \frac{8V}{3 \times \pi \times R^3 \times t}$$

where V is the quantity of liquid flowing, t is the time of flow, and R is the radius of the capillary tube. By means of curves made from the individual measurements, the relative viscosity at rates of flow of 200 and 1500 was established by interpolation. The percentage difference of the two values gives a more precise measure of the deviations from the Hagen-Poiseuille law shown by solutions of rubbers of different high average molecular weight: $\frac{\eta_{200} - \eta_{1500}}{\eta_{1500}} \times 100$.

It would be of interest to try to find simple relations between these deviations and the size of the molecule by a study of a larger quantity of substance, for it would then be possible to calculate the molecular weight of high molecular substances, *e. g.*, rubber of a molecular weight of 200,000 in an entirely different way. So far there has not been sufficient material for this purpose.

Three rubbers of different average molecular weights were studied in solutions of different concentrations for deviations from the Hagen-Poiseuille law. In all cases the deviation was less in dilute solution than in concentrated (see Table II).

TABLE II

DEPENDENCE IN PER CENT OF THE RELATIVE VISCOSITY AT MEAN VELOCITY OF FALL WITH DIFFERENT CONCENTRATIONS

	Molecular Base	η_r at Velocity of Fall 200	3000	$\frac{\eta_{200} - \eta_{3000}}{\eta_{3000}} \times 100$ in %
Fraction A Molecular weight 40,000	0.02	1.27	1.26	0.8
	0.05	1.59	1.56	2
	0.1	2.56	2.46	4
	0.2	4.64	4.30	8
Fraction B Molecular weight 60,000	0.02	1.34	1.32	1.5
	0.05	2.09	1.96	7
	0.1	3.90	3.25	20
	0.2	9.26	7.40	25
Fraction C Molecular weight 80,000	0.02	1.49	1.44	3.5
	0.05	2.48	2.11	18
	0.1	4.83	3.71	30
	0.2	12.40	8.96	38

These observations were also made with all colloidal molecules, especially polystyrenes. Dilute solutions, *i. e.*, sol solutions, in which the long molecules still do not interfere with one another, show slight deviations from the Hagen-Poiseuille law. In gel solutions these deviations are, on the contrary, greater and increase with the concentration, since the total sphere of action of the molecules compared with the volume of solvent available is steadily greater, and therefore the mutual interference of the molecules in the solution increases more and more.

In order to determine by viscosity measurements the molecular weight of the highest molecular rubber fraction, quite dilute solutions must be used, for then errors in the viscosity measurements resulting from deviation from the Hagen-Poiseuille law can be disregarded on account of the order of magnitude of the average molecular weight.[14] In types of rubber which have an average molecular weight of 40,000 and less, the deviations from the Hagen-Poiseuille law are so small that they can be disregarded in determinations of the molecular weight.

The deviations from the Hagen-Poiseuille law in rubber solutions, which lead to speculation[15] on the structure of rubber solutions, are explained in a very simple manner, and agree fully with other knowledge of colloidal molecules. The natural product, rubber, behaves the same as the synthetic polymer, polystyrene, so that a special structure need not be assumed for the former.

During the mastication of rubber[16] there is no destruction of the inherent structure, but the rubber is highly decomposed by atmospheric oxygen.[17] Masticated rubber has an average molecular weight of only 25,000 to 30,000[18] or less. Solutions of such small molecules behave normally. They are hemi-colloids whose solutions show no deviations from the Hagen-Poiseuille law, as has been proved in the case of numerous synthetic products.

Behavior of a Rubber Solution upon Agitation in the Light

As already mentioned, the deviations from the Hagen-Poiseuille law shown by rubber solutions have been ascribed to a special type of colloid particles in the solution. Such structures should be changed by agitation, as has been observed with numerous colloidal systems.[19]

TABLE III[20]

0.2-BASE MOLECULAR RUBBER SOLUTIONS IN TETRALIN AT 20° AND 60 CM. Hg

Fractions[21]	Molecular Weight	η_{sp} Directly after Solution[22]	η_{sp} after Agitating 100 Hours in the Dark	η_{sp} after Agitating 100 Hours in the Light
I	40,000	3.20	3.20	3.17
IV	100,000	10.07	10.24	9.89

Polystyrene solutions are not influenced[23] by shaking. On the contrary, if a solution of pure rubber is agitated, its viscosity diminishes greatly. This change in the viscosity is, however, a result of decomposition by atmospheric oxygen,[24] for if rubber is dissolved in air-free tetralin (0.2-base molar solution) and agitated with exclusion of air, the viscosity changes little or not at all. This is evidence against the view that the abnormal behavior of a rubber solution during viscosity measurements is due to an internal structure.

It has been observed many times that rubber is altered by light and that rubber in solution exposed to light has a much lower viscosity than that unexposed.[25] With complete exclusion of light the experiments in Table III show only a slight influence of light on a rubber solution. The earlier observations may be explained by the fact that light promotes the autoöxidation of rubber.[26]

Behavior of Rubber When Heated[27]

To test the stability of rubber solutions, 0.2-base molar solutions were heated in oxygen-free tetralin in an atmosphere of nitrogen for 100 hours at 60°. In all cases, with high as well as with low molecular rubber, this caused a marked degradation (Table IV). Polystyrene solutions of the same degree of polymerization are essentially more stable than these rubber solutions. The degradation is greatest in high molecular rubber. Accordingly after heating, rubber of a molecular weight of 200,000 yields cleavage fragments of the same average molecular weight as does rubber of a molecular weight of 100,000.

It is possible that heating causes cracking of the long molecular chains at the sensitive locations. It is, however, not impossible that at least a partial oxidation of the rubber occurs, for on weighing the rubber when the solution was prepared oxygen was never completely excluded. It is possible therefore that during the

weighing of the solid rubber there were formed on its surface small quantities of peroxides, which decompose in turn during solution and heating, and therefore bring about a cleavage of the chains. In order to carry out thoroughly reliable experiments on this decomposition, all the weighing would have to be done with exclusion of air.

TABLE IV

0.2-BASE MOLECULAR RUBBER SOLUTIONS IN TETRALIN AT 20° AND 60 CM. HG

Fractions	Molecular Weight	η_{sp} after Solution	η_{sp} after Heating 100 Hours at 60°
I	40,000	3.20	2.21
IV	100,000	10.07	7.61
VI	200,000	15.05	7.21

Behavior of Rubber Solutions toward Oxygen

In order to study the influence of a small quantity of oxygen, *e. g.*, air on rubber solutions, two kinds of rubber of different average degrees of polymerization (900 and 2000) were agitated and then heated in the presence of a little air and also in oxygen. The experiments were carried out in sealed vessels with 0.2-base molar solutions in tetralin. The volume of gas was about the same as the volume of the liquid. Parallel experiments were made at the same time with pure nitrogen. Even during solution there was a marked decomposition in the presence of air, and especially in the presence of oxygen. The viscosity of the rubber in the solvent containing air, as well as that containing oxygen, was much less after solution than when the experiments were carried out in nitrogen. This decomposition of the rubber during solution makes it very evident that solution is much more rapid in the presence of oxygen, and that rubber does not swell so greatly as in an atmosphere of nitrogen. The decomposed small molecules are more easily soluble than the larger ones; the swelling phenomena are especially pronounced only in the case of high molecular substances.[28] In order to dissolve high molecular rubber in an atmosphere of nitrogen, it must be agitated for three or four days. On the other hand, in the presence of air or oxygen it dissolves completely in one day. Masticated rubber which is considerably decomposed is likewise much more easily dissolved than unmasticated rubber (and without pronounced swelling effect), because there are highly decomposed molecules in masticated rubber. By prolonged agitation in the presence of oxygen, and particularly by heating, there is a further pronounced decomposition, and in fact both types of rubber that have a degree of polymerization of 2000 as well as that of 900 were decomposed by the prolonged action of oxygen to fragments of a degree of polymerization of approximately 150.

TABLE V

SPECIFIC VISCOSITY OF A 0.2-BASE MOLAR RUBBER SOLUTION IN TETRALIN AT 60 CM. HG PRESSURE

Molecular Weight about 50,000; Degree of Polymerization 750

	In N_2	In Dry CO_2	In Moist CO_2	In Air	In Oxygen
Viscosity after solution	4.78	5.08	4.75	3.92	3.0
After agitating 400 hours					
(*a*) in the dark	4.38	4.85	4.26	1.90	1.07
(*b*) in the light	..	4.45	4.15	1.59	1.01
Heated to 60°					
(*a*) 20 hours	4.08	4.42	4.45	1.73	0.64
(*b*) 100 hours	3.70	4.02	3.99	1.54	..
(*c*) 400 hours	3.53	3.84	3.16	1.29	0.60

This strong decomposition of rubber by oxygen has very frequently been described in the literature. Of course it was never followed in this way, since molecular weight determinations were not made previously in this simple manner. To determine the average molecular weight of the decomposed and of the undecomposed rubber, viscosity measurements as described in the following section were carried out in dilute solution, and from the $\frac{\eta_{sp}}{c}$ values obtained the molecular weight was established.

At the same time experiments were carried out on the behavior of rubber solutions toward both completely dried and moist carbon dioxide, for it was not considered out of the question that moist carbon dioxide, as a weak acid, has a destructive effect on rubber.

TABLE VI

Average Molecular Weight of Rubber about 140,000; Degree of Polymerization 2000

	In Nitrogen	In Dry CO_2	In Air	In Oxygen
Viscosity after solution	11.84	9.70	5.50	2.99
After agitating 400 hours				
(*a*) in the dark	...	8.62	4.52	1.31
(*b*) in the light	10.73[29]	8.38	3.86	1.09
Heated to 60°				
(*a*) 20 hours	10.58	9.00	3.42	1.67
(*b*) 100 hours	10.20	8.27	2.99	0.76
(*c*) 400 hours	9.10	7.28	2.81	0.72

TABLE VII

MOLECULAR WEIGHT DETERMINATIONS OF LOW MOLECULAR RUBBER AND ITS DECOMPOSITION PRODUCTS

Kind of Rubber	Base Molarity of the Solution	η_{sp}	$\frac{\eta_{sp}}{c}$	Molecular Weight $\frac{\eta_{sp}}{c \times K_m}$ ($K_m = 3 \times 10^{-4}$)	Degree of Polymerization
Original rubber	0.02	0.32	16.0	53,000	750
Heated 400 hrs. in N_2 at 60°	0.02	0.23	11.5	38,000	550
The same in O_2	0.04	0.12	3.0	10,000	150

TABLE VIII

MOLECULAR WEIGHT DETERMINATION OF HIGH MOLECULAR RUBBER AND ITS DECOMPOSITION PRODUCTS

Kind of Rubber	Base Molarity of the Solution	η_{sp}	$\frac{\eta_{sp}}{c}$	Molecular Weight $\frac{\eta_{sp}}{c \times K_m}$ ($K_m = 3 \times 10^{-4}$)	Degree of Polymerization
Original rubber	0.02	0.85	42.5	142,000	2000
Heated 400 hrs. in N_2 at 60°	0.02	0.59	29.5	98,000	1400
The same in O_2	0.04	0.14	3.5	11,700	170

According to Tables V and VI, a carbon dioxide solution has no appreciable effect on the viscosity of a rubber solution. This result is of interest since Pummerer[30] states, according to experiments by von Kroepelin and Brumshagen, that the viscosity of a sol rubber solution after heating for five days at 60° with carbon dioxide increased one and one-half times and besides showed a structural viscosity. This observation could not be confirmed by the authors.[31]

Molecular Weight Determinations of Rubber[32]

If the viscosity of a rubber solution is determined at different temperatures, the viscosity at 60° is somewhat less than that at 20°. Upon cooling, the original

value is no longer obtained, which indicates that decomposition has occurred even with a short period of heating at 60°.

TABLE IX

η_{sp} IN 0.2-BASE-MOLAR TETRALIN SOLUTION AT 60 CM. PRESSURE AT DIFFERENT TEMPERATURES

	High Molecular Rubber	Rubber with Average Molecular Weight	Low Molecular Rubber
20°	9.7	4.78	0.72
Heated to 60°	9.11	4.75	0.68
Cooled to 20°	9.03	4.20	0.71

If the specific viscosity in different concentrations of the sol region is determined, the $\frac{\eta_{sp}}{c}$ values, from which the molecular weight is calculated, are not constant, but deviate to a slight extent. This depends upon the sensitivity of the solutions, which makes it difficult to obtain exactly reproducible values.

In Table X the $\frac{\eta_{sp}}{c}$ values are given for the same velocity of fall and again at 10 cc. Hg, since there are slight deviations from the Hagen-Poiseuille law. The differences which are given here are not considerable, since the deviations from the Hagen-Poiseuille law in the sol region are very slight.

TABLE X

MEASUREMENTS IN TETRALIN SOLUTION AT 20°

Base Molecular	η_{sp} at 10 Cm. Hg	$\frac{\eta_{sp}}{c}$ at 10 Cm. Hg	$\frac{\eta_{sp}}{c}$ At a Velocity of Fall of 200	$\frac{\eta_{sp}}{c}$ At a Velocity of Fall of 3000
	Fraction A: Mol. Wt. around 40,000			
0.02	0.27	13.5	13.5	13.0
0.05	0.59	11.8	11.8	11.2
0.1	1.55	15.5	15.6	14.6
0.2	3.60	18.0	18.2	16.5
	Fraction B: Mol. Wt. around 60,000			
0.02	0.34	17.0	17.0	16.0
0.05	1.07	21.4	21.8	19.2
0.1	2.69	26.9	29.0	22.5
0.3	8.12	40.6	41.3	32.0
	Fraction C: Mol. Wt. around 80,000			
0.02	0.49	24.5	24.5	22.0
0.05	1.33	26.6	29.6	22.2
0.1	3.55	35.5	38.3	27.1
0.2	10.50	52.5	57.0	39.8

At higher concentrations the viscosity no longer increases proportionally, but disproportionately so; in fact the higher the molecular weight of the rubber the greater is this increase. The very same observations were made with polystyrenes. The relation between viscosity and concentration is only very incompletely expressed by the Arrhenius formula: $\frac{\log \eta_r}{c} = K_c$. The K_c values show a very considerable change. Since solutions of high concentration have greater deviations from the Hagen-Poiseuille law, the K_c values were determined at such velocities of fall without better results being obtained. It is, therefore, interesting that with the

highest velocities of fall the change of the K_c constant is greater than at slight velocities.

Molecular weight determinations of polystyrenes were made according to two methods: first, on the basis of the relation: $\frac{\eta_{sp}}{c} = M \times K_m$, where the viscosity determinations had to be made in very dilute solution and, second, according to another formula:

$$M = K_c \times K_{cm} \; (K_{cm} = \text{about } 10^4)$$

TABLE XI

Base Molar	At 10 Cm. Hg η_r	At 10 Cm. Hg K_c	At Velocity of Fall of 200 η_r	At Velocity of Fall of 200 K_c	At Velocity of Fall of 3000 η_r	At Velocity of Fall of 3000 K_c
			Fraction A			
0.02	1.27	5.19	1.27	5.19	1.26	5.02
0.05	1.59	4.03	1.59	4.03	1.56	3.86
0.1	2.55	4.07	2.56	4.08	2.46	3.91
0.2	4.60	3.31	4.64	3.33	4.30	3.17
			Fraction B			
0.02	1.34	6.35	1.34	6.35	1.32	6.03
0.05	2.07	6.32	2.09	6.40	1.96	5.85
0.1	3.69	5.67	3.90	5.91	3.25	5.12
0.2	9.12	4.79	9.26	4.83	7.40	4.35
			Fraction C			
0.02	1.49	8.66	1.49	8.66	1.44	7.92
0.05	2.33	7.35	2.48	7.88	2.11	6.49
0.1	4.55	6.58	4.93	6.84	3.71	5.69
0.2	11.50	5.30	12.40	5.47	8.96	4.76

To determine the K_c values, the measurements could be made in a higher concentration of the mixtures as a rule. Both formulas are related to one another, since the same series of viscosity measurements was used to calculate the molecular weights. Since with rubber neither the $\frac{\eta_{sp}}{c}$ values nor the K_c values are constant, the molecular weight can be estimated only in a rough way. Accordingly, the measurements were made in rather dilute solution, because the mutual interference of the molecules is then of least importance. The molecular weight was calculated by both formulas, resulting in approximately the same values, as shown in Table XII, if the average of the mean of the K_c values is taken as a basis for the molecular weight determination.

TABLE XII

Fractions	K_c Average	$M = K_c \times K_{cm}$ $K_{cm} = 10^4$	η_{sp} in 0.02-Base Molar Solution	$\frac{\eta_{sp}}{c}$	$\frac{M = \eta_{sp}}{c \times K_m}$
A	4.2	42,000	0.27	13.5	45,000
B	5.9	59,000	0.34	17.0	58,000
C	7.2	72,000	0.49	24.5	82,000

Comparison of Raw, Purified, and Synthetic Rubber

The preceding viscosity measurements show that purified rubber is extraordinarily sensitive to oxygen. In order to prevent changes in the rubber solutions, oxygen must be excluded most carefully. On the contrary, solutions of raw rubber, *e. g.*, crepe rubber and Para rubber, behave very differently. They are much more stable and are only slowly changed by air. This depends upon the fact that natural rubber contains anticatalysts which retard autoöxidation.

It has already been proved by different investigators that rubber extracted with acetone is extraordinarily more sensitive to oxygen than unextracted rubber.[33] The products purified by Pummerer are especially sensitive to oxygen. As is known, synthetic rubber is also very easily autoöxidized, because it is free from anticatalysts. The knowledge and use of antioxidation is therefore in this case of great importance in order to stabilize the rubber.[34] The influence of these antioxidants on the stability of rubber is very important. As is well known, natural rubber can be stored for a long time without undergoing essential modifications.[35] Only very slowly is rubber changed by oxidation into insoluble rubber, which can finally be decomposed by further oxidation so that it becomes greasy and is again soluble.[36] This decomposition takes place very rapidly with purified and synthetic rubber, so that samples are completely changed after standing only a short time. This different behavior cannot be explained, as has been supposed, by differences in the state of aggregation of natural, purified, and synthetic rubber, but solely by the anticatalysts which are present in natural rubber. Bruson has isolated some high molecular substances from latex which he considers antioxidants.[37] With the aid of viscosity measurements, the action of these anticatalysts should be investigated further, for it offers a convenient means of studying the oxidative decomposition of rubber.

TABLE XIII

DECOMPOSITION OF A RAW RUBBER OF A MOLECULAR WEIGHT OF 130,000

		η_r				
		Immediately	After Days			
% Content	Base Molar	after Solution	6	10	40	60
0.25	0.0367	2.97	2.89	2.85	2.81	2.79
0.5	0.0735	7.46	7.13	6.76	6.66	6.47
1	0.147	30.03	26.88	24.72	23.35	..

TABLE XIV

		η_r				
% Content	Base Molar	At 20°	At 40°	At 60°	At 75°	Cooled again to 20°
0.25	0.0367	2.82	2.79	2.80	2.77	2.82
0.5	0.0735	6.58	6.54	6.54	6.44	6.57
1	0.1470	23.35	23.27	22.98	23.40	23.31

As an example of the great stability of natural rubber, the following viscosity measurements may be cited: Foll studied changes in viscosity of benzene solutions of *Hevea* rubber on standing, in other words, the decomposition of rubber by oxygen.[38] According to Table XIII the autoöxidation proceeds extraordinarily slowly.

After standing for 60 days' there is hardly any decomposition of the raw rubber in a 0.25% (0.0367 base molar) solution, whereas according to our experiments a solution of a purified rubber of about the same molecular weight was decomposed to a molecular weight of 30,000.

Foll has observed further that the relative viscosity of a raw rubber solution changes very little on heating from 0° to 75°, and after cooling it again becomes as viscous as the original solution (see Table XIV). This study proves that the colloid particles are not changed upon heating, and therefore that the colloid particles of rubber are molecules and not micelles. On account of the anticatalysts it contains, a raw rubber solution is accordingly as stable as solutions of polystyrenes.[39]

The calculated average molecular weight of this rubber is:

$$M = \frac{\log \times \eta_r}{c} \times K_{cm} = \text{about } 120{,}000$$

based on the η_r values at the lowest concentration.

Finally, one of the numerous measurements of van Rossem,[40] which shows the rise in viscosity with increasing concentration, was made in an Ostwald viscosimeter, that is, at a very different velocity of fall. In dilute solutions of low viscosity the velocity of fall is much greater than in concentrated solutions of high viscosity. The K_c constant here has only a slight change; at higher velocities of fall the relations between viscosity and concentration can no longer be expressed by the Arrhenius formula. As is shown in Table XV, the change of the constant K_c is greater at greater velocities of fall than at smaller velocities.

TABLE XV

% Content	Base Molar	η_r	η_{sp}	$\frac{\eta_{sp}}{c}$	$K_c = \frac{\log \eta_r}{c}$
0.10	0.0147	1.7	0.7	47.6	15.6
0.20	0.0294	3.0	2.0	68.0	16.2
0.22	0.0323	3.3	2.3	71.2	16.1
0.25	0.0367	3.9	2.9	79.0	16.1
0.30	0.0441	5.0	4.0	90.7	15.8
0.40	0.0588	7.6	6.6	112.2	15.0
0.43	0.0632	8.6	7.6	120.3	14.8
0.45	0.0661	9.2	8.2	124.0	14.6
0.50	0.0735	11.6	10.6	144.2	14.5
0.60	0.0882	15.5	14.5	164.4	13.5
0.70	0.1029	20.7	19.7	191.4	12.8
0.80	0.1176	27.4	26.4	224.4	12.2
0.87	0.1280	39.5	38.5	300.8	12.5
0.90	0.1323	38.8	37.8	285.7	12.0
1.00	0.1470	59.5	58.5	398.0	12.1

From the constant K_c, a molecular weight of about 150,000 was calculated for these rubbers, *i. e.*, an average degree of polymerization of about 2000. The decomposition of the rubber in light and in air, which is influenced by catalysts of which the composition and mode of action are still unknown, accounts for the widely differing ideas on aging phenomena and the processes of mastication. All these processes may now be studied more closely, for if all changes in rubber are attributable to chemical reactions, *i. e.*, to a decomposition of the molecule, these processes can be clearly described, and the vague ideas now unfortunately prevalent can be avoided in the future.

Latex an Emulsoid

H. Staudinger, J. Joseph, and E. O. Leupold[41]

A comparison of latex with solutions of rubber in organic solvents shows a difference between the two very different sorts of colloid systems which were both designated as emulsoids previously. It was formerly considered that there was an essential difference between latex and a rubber solution in benzene, in that in the first case the particles are not solvated, whereas in organic solvents a strong solvation of the micellar colloid particles was considered to exist. Latex, however, consists of an emulsion of rubber particles in an aqueous medium;[42] if an emulsion is a colloidal system in which a liquid phase is dispersed in a liquid dispersing medium, then latex is an emulsoid. Latex has low viscosity. Ordinary *Hevea* latex contains as a rule 25–30 per cent rubber, and therefore is 4–5 times base molar, calculated on the C_5H_8 residue. The content was determined by precipitation, solutions of known

content were then prepared by dilution, and the viscosity of base molar latex and of even more dilute emulsions was measured. For this purpose old latex was used, which yielded almost nothing but insoluble rubber and fresh latex which in turn yielded soluble rubber. The differences in the viscosity of the two were not large, and at this time no further conclusions can be drawn from them.

TABLE XVI

VISCOSITY OF HEVEA LATEX

Base Molar	Content in %	Old Latex			Fresh Latex		
		η_{sp}	$\frac{\eta_{sp}}{c}$	$K_c = \frac{\log \eta_r}{c}$	η_{sp}	$\frac{\eta_{sp}}{c}$	$K_c = \frac{\log \eta_r}{c}$
0.125	0.85	0.03	0.24	0.10	0.02	0.16	0.07
0.25	1.7	0.08	0.32	0.13	0.05	0.20	0.07
0.5	3.4	0.17	0.34	0.13	0.11	0.22	0.09
1.0	6.8	0.39	0.39	0.14	0.24	0.24	0.09
2.0	13.6	1.05	0.52	0.15	0.58	0.29	0.10

A comparison of these with solutions of rubber in organic solvents shows the extraordinarily high viscosity of the latter solutions. Based on the average molecular weight, solutions of rubber in benzene or tetralin have $\frac{\eta_{sp}}{c}$ values of 30–70; solutions of latex, on the contrary, have only 0.2–0.4. A 0.25-base molar rubber solution, *i. e.*, a 1.7 per cent solution, has a relative viscosity of 10–30; a latex of the same concentration only 1.08. The almost spherical particles of latex therefore increase the viscosity of the solution to no great extent, since the sphere of action of the colloid particles is approximately the same as their own volume. In a solution of rubber in benzene, however, the long molecules are dissolved separately, and the sphere of action of these fiber molecules is much greater than their own volume. This in turn explains the enormously high viscosity of their solutions. Accordingly, the difference between latex and benzene solutions of rubber does not depend upon differences in solvation, but on the fact that spherical particles are suspended in latex, while in a rubber solution long molecules (fiber molecules) are dissolved. As was explained earlier,[43] it is not necessary to assume a special solvation; instead, during solution of the rubber molecules in benzene, an approximately monomolecular solvate layer is formed around the molecules. The magnitude of the solvate layer does not therefore account for the high viscosity, as Fikentscher and Mark[44] believe, but the large sphere of action of the long molecules.[45] As an emulsion, latex shows a normal rate of flow. The viscosity of a slow and quickly flowing liquid is the same, since they have spherical shaped particles, and there is therefore no mutual interference.

TABLE XVII

LATEX AT DIFFERENT PRESSURES, MEASURED IN THE UBBELOHDE VISCOSIMETER

Pressure in Cm. Hg	Old Latex, Base Molar		Fresh Latex, Base Molar	
	η_r in 1 G. Mol.	η_r in 2 G. Mol.	η_r in 1 G. Mol.	η_r in 2 G. Mol.
10	1.39	2.05	1.25	1.59
30	1.39	2.05	1.24	1.58
60	1.37	2.03	1.24	1.56

The idea that strongly solvated micelles are present in a rubber solution was suggested earlier by a comparison with soaps, which also form highly viscous solutions and which do not obey the Hagen-Poiseuille law. It is possible that with soaps also the high viscosity is due less to the strong solvation of the molecules than

to the long form of the micelles; this long form in turn governs the deviations from the Hagen-Poiseuille law. This will be reported in another article.

References

[1] *Ber.*, **60**, 2152 (1927).

[2] Staudinger and Leupold, *Ibid.*, **63**, 730 (1930).

[3] Kirchhof, *Kolloid-Z.*, **15**, 31 (1914).

[4] Hess, *Ibid.*, **27**, 1, 154 (1920); Hatschek, *Ibid.*, **13**, 88 (1913); Ostwald, *Ibid.*, **27**, 1, 154 (1920).

[5] *Kolloid-Z.*, **53**, 239 (1930).

[6] Ostwald, *Ibid.*, **36**, 99, 248 (1925); **43**, 190 (1927).

[7] Staudinger and Machemer, *Ber.*, **62**, 2926 (1929); *Kolloid-Z.*, **51**, 87. In the illustration, polystyrenes 5 and 4 are unfortunately interchanged. Polystyrene 4 with the higher molecular weight shows a greater deviation from the Hagen-Poiseuille law than does polystyrene 5.

[8] Staudinger and Bondy, *Ber.*, **63**, 728 (1930).

[9] Signer, *Pharm. Chem.*, **150A**, 257 (1930).

[10] The deviations of soap solutions are due to the elongated micelles in the solution.

[11] In earlier works we expressed the deviation from the Hagen-Poiseuille law by the formula: $\frac{\eta_{10} - \eta_{60}}{\eta_{10}} \times 100$. The deviations were more noticeable according to the above formula. *Ber.*, **63**, 727 (1930).

[12] Kroepelin, *Ibid.*, **62**, 3062 (1929).

[13] The η_r values for velocities of fall of 200 and 1500 were read from the curves.

[14] In this low concentration the measurement is made at the dead velocity of fall. Under these conditions the relative viscosity changes but little with the velocity of fall, so that the mixtures of the different products are comparable with one another.

[15] Dogadkin and Pewsner, *Kolloid-Z.*, **53**, 239 (1930).

[16] Harries, *Ibid.*, **33**, 183 (1923). From viscosity measurements of such plasticized rubber, it can be assumed that this rubber no longer represents the original dispersed phase or an aggregation, but that it is disaggregated. Probably mechanical plasticization disturbs or prevents the mutual adsorption of two or more disperse phases which, according to Wo. Ostwald, are present in ordinary natural rubber. Mechanical plasticization therefore has an effect similar to the peptizing action of organic acids.

[17] Staudinger, "Process for the Mastication of Rubber in Vacuo with Oxygen." Swiss Patent 119,027 (Nov. 25, 1925).

[18] *Ber.*, **63**, 921 (1930).

[19] Freundlich, *Ibid.*, **61**, 2227 (1928).

[20] In the measurements of this table, as in all the following measurements, only the η_{sp} values at 60 cm. pressure are given. For more exact knowledge the η_{sp} value at the same velocity of fall must be compared. Still the differences are not very appreciable, so that the above values are satisfactory for this tentative data.

[21] The preparation of the rubber fractions is described in the following work.

[22] To complete solution, the rubber must be agitated with tetralin about three to six days.

[23] Staudinger and Frey, *Ber.*, **62**, 2909 (1929).

[24] See Tables V and VI.

[25] van Rossem, *Kolloidchem. Beihefte*, **10**, 101 (1918).

[26] Experiments by Leupold.

[27] Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[28] Staudinger, *Kolloid-Z.*, **54**, 135 (1931).

[29] The slight decomposition is possibly to be attributed to the fact that oxygen has been absorbed by the substance during weighing.

[30] "Handbuch der Kautschukwissenschaften," **1930**, page 211.

[31] In a few experiments we noticed that insoluble rubber separated on heating a rubber solution. Perhaps under special conditions a union of the long chains by oxygen bridges to 3-dimensional molecules can take place. In this case the viscosity of a solution might increase before the separation of insoluble rubber occurs.

[32] *Ber.*, **63**, 734, 921 (1930).

[33] Peachey, *J. Chem. Soc.*, **31**, 1103 (1913); Stevens, *J. Soc. Chem. Ind.*, **35**, 874 (1916); Beadle and Stevens, *Gummi-Ztg.*, **27**, 1907 (1913); Peachey and Leon, *India Rubber J.*, **54**, 1850 (1918).

[34] Beadle and Stevens, *J. Soc. Chem. Ind.*, **31**, 1099; Gottlob, *Gummi-Ztg.*, **30**, 303, 326 (1916).

[35] For the change in rubber on standing, see Bary, *Chem. Zentr.*, **1927**, II, 514.

[36] Bary and Fleurent, *Compt. rend.*, **184**, 947 (1927).

[37] Bruson, *Ind. Eng. Chem.*, **19**, 1187 (1927).

[38] *Kolloid-Z.*, **12**, 144 (1913); Woudstra, *Ibid.*, **5**, 31 (1909).

[39] Staudinger and Heuer, *Ber.*, **62**, 2933 (1929).
[40] See Note 25.
[41] Leupold, *Thesis*, Freiburg, **1931**.
[42] Staudinger, *Ber.*, **62**, 2398 (1929).
[43] Staudinger and Heuer, *Ibid.*, **62**, 2933 (1929).
[44] *Kolloid-Z.*, **49**, 135 (1929).
[45] Staudinger, *Ber.*, **63**, 921 (1930).

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Isoprene and Rubber

Part 35. Soluble and Insoluble Rubber and the Fractionation of Rubber

H. Staudinger and H. F. Bondy

Conversion of Insoluble Rubber to Soluble Rubber

According to the views of earlier authors, the transformation of insoluble rubber to soluble rubber is reversible.[1] Bary and Hauser speak of an equilibrium between the α and β forms which takes place rapidly. The reversion of insoluble rubber to soluble rubber is brought about by mastication, by chloroacetic acid and other acids, and finally also by standing in air. The fact was completely overlooked that the soluble rubber thus obtained has quite different properties from the original rubber. Its solutions have a low viscosity. Accordingly it is not a question of a reversion from insoluble to soluble rubber, but of a degradation. The conversion of insoluble to soluble rubber is a result of a cleavage of the molecules of insoluble rubber by reagents such as chloroacetic acid and oxygen, and finally during mastication. The 3-dimensional molecules of the insoluble rubber, which are composed of long fiber molecules of soluble rubber, are broken up in this degradation into short fragments which are also fiber molecules and therefore dissolve. The soluble rubber obtained by decomposition is of a hemi-colloidal character, and is not the original high molecular soluble rubber.

A similar decomposition also takes place with further autoöxidation; the insoluble rubber passes rather quickly to degraded soluble rubber when it is heated in the strongly swollen state at 60° in the presence of air. Insoluble rubber is also rendered soluble by strong mastication. Here, too, there is a degradation by oxidation. Naturally it is also possible that a direct mechanical rupture of the chains takes place. A deeper insight into the process of mastication will be had only if rubber is masticated with the most careful exclusion of air.

Most chemical reactions of rubber, *e. g.*, the action of bromine, hydrochloric acid, nitrosobenzene, and nitrous acid take place, as already found, with extensive decomposition of the chains.[2] The transformation products of rubber are as a rule derivatives of hemi-colloidal decomposition products. As a result of this extensive decomposition, both soluble rubbers and insoluble rubbers yield the same reaction product. The few bonds of union which link the long chains of soluble rubber to the 3-dimensional macromolecules of insoluble rubber can no longer be detected analytically in the decomposed products of the reaction. The physical properties, especially the solubility, are influenced to a high degree by the union of the long fiber molecules to 3-dimensional molecules, but this is not true of the chemical behavior, since most of the isoprene residues in the rubber chains remain unchanged after the union.

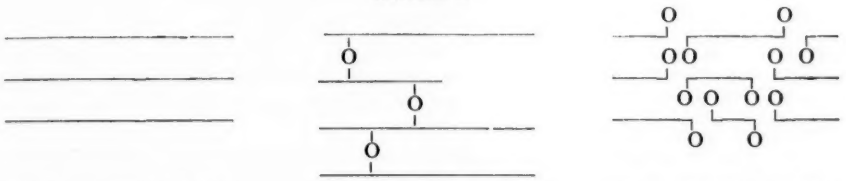
The changes from soluble to insoluble rubber are therefore not irreversible, as Bary and Hauser[3] assume. They do not depend on changes in the state of aggregation, *i. e.*, colloidal phenomena, which leave the real rubber molecule unchanged, but they depend upon chemical transpositions of the unsaturated and very unstable macromolecules of rubber. The transposition between the different kinds of rubber is therefore not expressed according to Scheme 1, as Bary and Hauser believe, but by Scheme 2.

SCHEME I

α-rubber $\rightleftharpoons$ β-rubber

Soluble with swelling — Insoluble, swells greatly

SCHEME 2



High molecular soluble rubber; Fiber molecules of a degree of polymerization of 1000–2000 → Insoluble rubber; 3-dimensional macromolecules, which consist of a union of fiber molecules with a few oxygen atoms. Only swells → Decomposed soluble rubber of a degree of polymerization of 200–400; formed from 3-dimensional molecules by oxidative cracking

The Structure of Latex Particles

These new views of the structure of soluble and insoluble rubber lead to the following picture of the structure of the latex particle. Freundlich and Hauser[4] have shown that the enveloping substance of latex particles has a different consistency from the inside. In this case the insoluble skin might be formed by conversion of the fiber molecules on the outside of the latex particles into 3-dimensional molecules by autoöxidation. In favor of this is the fact that old latex that has been standing for a long time yields much more insoluble rubber than does fresh latex. A rapid autoöxidation of rubber in latex is retarded by antioxygens. It would be of interest to study types of rubber from different plants for their content of soluble rubber and of antioxygens. According to investigations by Caspari[5] the quantity of insoluble rubber in a given type of rubber varies greatly. Exact results will be obtained only if the latex is tapped with complete exclusion of air. In this case it might also possibly be learned whether the skin substance observed by Hauser is formed later by autoöxidation.

Our investigations have proved, furthermore, that soluble rubber is a mixture of homologous polymers. This does not mean that the soluble part of the latex particles consists of such a mixture. With the sensitiveness of rubber it is not impossible that during purification, according to the method of Pummerer, a decomposition of the long rubber chains takes place. It is therefore possible that the easily soluble low molecular parts of the rubber are not present originally, but are secondary decomposition products. It is conceivable that natural macromolecules represent a very definite uniform length of chain and not mixtures of homologous polymers. This question can be decided only if rubber latex is tapped with the most careful exclusion of air, and if a new fractionation of the rubber is made. In the case of all high molecular natural products the same question can be raised; namely, whether they consist of a mixture of homologous polymers like synthetic high polymers, or whether nature can produce long molecules of uniform length of chain. This question, which is so important in advancing the knowledge of high molecular natural products, has not up to now been settled in any case, *e. g.*, for rubber, gutta-percha,[6] cellulose,[7] or albumin.

EXPERIMENTS

Fractionation of Rubber

According to our concept, soluble rubber consists of a mixture of homologous polymeric polyprenes, *i. e.*, of fiber molecules of various lengths. Such a mixture can be separated by fractional solution or precipitation into higher and lower molecular parts.[8] The process of such a separation can be followed by a comparison of the viscosities of solutions of the same concentration, for the difficultly soluble high molecular components give solutions of higher viscosity than the more easily soluble low molecular ones.

This plan of operation is based on numerous experiments with synthetic high polymeric hydrocarbons.[9] Thus high molecular polystyrene consists of a mixture of products of widely different degrees of polymerization. The low molecular components can be separated from the higher ones, for example, by extraction with acetone. From a polystyrene of an average molecular weight of 100,000, easily soluble low molecular components of an average molecular weight of 10,000 can be obtained; the most difficultly soluble components have a molecular weight of 200,000 or more.[10]

In these, as in other cases, the individual fractions were distinguished by the viscosities, and the average molecular weight was determined by viscosity measurements.[11] Gutta-percha also can be separated into higher and lower molecular components in a similar way by fractional precipitation.[12]

The first experiments on the fractionation of rubber gave results which were contradictory to our concept of the structure of rubber. Apparently they can be very well explained on the basis of the views of Pummerer, Meyer, and Mark, and other investigators, *i. e.*, on the assumption of a micellar structure of rubber.

Fractionation of Rubber by the Method of Pummerer

A rubber purified by the method of Pummerer, Andriessen, and Gündel[13] was extracted with ether in an atmosphere of carbon dioxide and the ether was changed frequently in order to obtain a fractional extraction. After the ether-soluble rubber was removed, 10 per cent of ethyl bromide was added to the ether, which brought all of the rubber gradually into solution.

The individual rubber fractions were obtained by evaporation of the solvent *in vacuo*. Only fractions I to IV were soluble in benzene. The viscosity of solutions of these fractions of like concentration increased; consequently there had been a fractionation of the rubber into higher and lower molecular parts. After evaporation of the solvent and drying of the residues for one week in a high vacuum, fractions V to X were insoluble in benzene and merely swelled strongly in this solvent. Soluble rubber had been converted into insoluble rubber. This transformation therefore takes place especially easily in the case of the higher molecular fractions, which agrees with many later observations.

Strange to say, upon prolonged agitation with pure bromobenzene in light all the fractions, including the insoluble rubber, dissolved. Morever the viscosity of all the fractions in bromobenzene were approximately the same (see Table I). This phenomenon can be explained on the assumption that the rubber micelles, which originally differed through their state of aggregation, were split up by the bromobenzene so that in the end micelles of the same size are dissolved in bromobenzene. In this connection Pummerer, Nielsen, and Gündel[14] assumed that sol and gel rubber are dispersed in the form of particles of the same size in camphor and menthol.

TABLE I

Fractions	Grams	Extraction Time	Solubility in Benzene	Appearance	η_{sp} 0.25-Base Molar Solution: In Benzene	η_{sp} 0.25-Base Molar Solution: In Bromobenzene
Unfractionated	50	.....	Not completely	Light brown	..	2.30
I	6	6 hours	Easily		3.85	2.50
II	13	18 hours	Easily		4.12	2.81
III	6	1 day	Easily	Yellow	4.88	2.65
IV	3	1 day	Difficultly		5.26	2.62
V	4	2 days	Difficultly		Swells greatly, not entirely dissolved	2.50
VI	2	3 days	Difficultly	Yellow and barely transparent	Strong swelling	2.54
VII	2	7 days	Not soluble			2.81
VIII	1	9 days	Not soluble			2.88
37 grams of ether-soluble sol rubber (Pummerer's method)						
IX	0.5	6 hours	Insoluble	Brown and opaque	Strong swelling	2.47
X	4	1 day	Insoluble			2.51
XI	2.5	3 days	Insoluble			2.30

7.0 grams of ether-insoluble gel rubber (Pummerer's method).
Total decomposition 44 grams—6 grams lost during the experiment.
Extraction medium for I–VIII, ether, for IX–XI, ether + 10 per cent ethyl bromide.

We have now proved that in solutions of rubber and camphor there is an advanced degradation to hemi-colloidal polyprenes.[15] With these fragments no difference can be distinguished between sol and gel rubber. In bromobenzene solutions there is, according to our point of view, no disaggregation of micelles, but rather a cleavage of molecules; in fact, under the influence of light, bromobenzene is decomposed with formation of bromine and hydrogen bromide,[16] and these latter reagents bring about a cleavage of the rubber molecules. Even the 3-dimensional molecules of insoluble rubber are decomposed in this way and converted into 1-dimensional molecules. The decomposition of rubber chains by bromine and hydrogen bromide has been dealt with in another work,[17] in which case the longer molecules are more easily broken up than the shorter ones. The same phenomena are true of polystyrenes.[18] Therefore, by the action of bromine on polystyrenes of widely different average molecular weight, fragments of approximately the same average molecular weight are obtained. It is therefore not surprising that upon prolonged treatment in bromobenzene the different large rubber molecules are broken up into fragments of the same size. That upon solution in bromobenzene an irreversible decomposition of the molecules and not a disaggregation of the micelles takes place is shown by viscosity measurements at different temperatures. The specific viscosity of a 0.25-base molar rubber solution in benzene diminished somewhat upon heating from 20° to 60° C. When cooled to 20°, the viscosity returns to its original value; consequently the phenomenon is reversible. In bromobenzene, however, there is an ir-

TABLE II

η_{sp} OF A SOL RUBBER OF A MOLECULAR WEIGHT OF ABOUT 35,000 IN 0.25-BASE MOLAR SOLUTION

	20°	40°	60°	Cooled to 20°
In benzene	5.75	5.50	5.28	5.70
In bromobenzene	5.46	5.13	4.84	4.50

reversible decomposition of the molecules of the heated solution, for after cooling the heated solution has a lower viscosity than before. Naturally the experiments must be carried out with the most careful exclusion of oxygen.

To follow the decomposition of rubber fractions of different sizes by bromobenzene, easily and difficultly soluble sol rubbers were dissolved in bromobenzene and tetralin and the viscosities of these solutions in 0.2-base molar solution at 27° were compared. In bromobenzene the viscosity of the higher fractions was less than in tetralin because of the decomposition. However, the decomposition was not far advanced, so that the viscosities of all the fractions were the same.

TABLE III

VISCOSITIES OF RUBBER FRACTIONS AT 20° AND 60 CM. Hg

Rubber Fractions	Molecular Weight	η_{sp} in 0.2-Base Molar Tetralin Solution	η_{sp} in 0.2-Base Molar Bromobenzene Solution
I	43,000	3.20	3.21
III	72,000	7.29	4.69
IV	100,000	10.07	4.32
VI	225,000	15.05	9.00

Second Fractionation of Rubber by the Method of Pummerer

The foregoing experiment was repeated, except that methylene chloride was added instead of ethyl bromide to dissolve the ether-soluble part of the rubber. For, like bromobenzene, ethyl bromide decomposes in light and therefore brings about a decomposition of the rubber during extraction.[19]

To isolate the rubber fractions, the individual solutions (after concentrating) were poured into methyl alcohol, whereupon the rubber separated. Under these conditions all the fractions were still soluble in benzene, even after several weeks' drying in high vacuum. The viscosities in 0.25-base molar tetralin solution of all the fractions were measured in an Ostwald viscosimeter. Table IV shows, as was to be expected, that Fractions I to V have different molecular weights, judged by their viscosities. The more difficultly soluble rubber had a higher molecular weight than the more easily soluble rubber. However, from Fractions VI on the viscosity diminished again, especially when the extraction agent was methylene chloride.

TABLE IV

Fractions	Grams	Time of Extraction (Days)	η_r in 0.25-Base Molar Solution (Tetralin)	Analyses % C	Analyses % H
Unfractionated	50	..	Not completely soluble	88.12	11.70
I	0.6	1/4	10.00		
II	6	3/4	12.99	87.77	11.83
III	7	2	13.58	...	...
IV	3	2	18.32	...	...
V	6	5	27.20	...	...
VI	2	5	23.20	87.98	11.73
VII	2	10	8.40	88.01	11.75
26.6 grams of ether-soluble sol rubber (Pummerer's method)					
VIII	4	2	9.60	88.16	11.65
IX	12	2	9.60	88.10	11.74

16 grams of ether-insoluble gel rubber (Pummerer's method).

Total amount decomposed: 42.6 g.; 7.4 g. lost during precipitation of the fractions.

I–VII were extracted with ether, VIII with ether-methylene chloride 1 : 1, and IX with methylene chloride.

It might seem as if the ether-insoluble rubber yielded solutions of lower viscosity after it was once dissolved than did the ether-soluble rubber. However this is not the case. Here, too, there was degradation of the rubber, either as a result of the action of the solvent or by oxygen which was dissolved in the solvent, or as a result of prolonged heating in the solvent during extraction. It should be noted however that in this experiment, too, the operations were carried out in carbon dioxide but that the solvent was not free from air. There is no difference in the individual fractions (Table IV).

Fractionation of Rubber in the Cold

The sensitivity of the highest molecular rubber at elevated temperatures suggested that a decomposition during prolonged heating causes combination.

Accordingly, purified rubber was extracted in the cold first with ether and then with benzene. The ether was dropped slowly from a flask on to the bottom of the extraction vessel and it then flowed off into another flask through an overflow. As soon as the upper flask was empty both flasks were changed. In this way the solvent was passed through the rubber numerous times. After exhaustive extraction with ether it was extracted with benzene and the rubber was then almost entirely dissolved. To recover the rubber, the solution was concentrated *in vacuo*, and the rubber was precipitated by pouring the solution into methyl alcohol.

TABLE V

Fractions	Grams	Time of Extraction (Days)	η_r in 0.25-Base Molar Solution (Tetralin)	Analyses % C	Analyses % H
Unfractionated	40		Not completely dissolved		
I	3	3/4	16.88	87.98	11.70
II	4	2	18.75	...	...
III	7	4	20.88	88.12	11.80
IV	5	4	14.08	88.18	11.96
V	4	4	12.08	88.26	11.81
VI	4	8	9.60	88.34	12.04
VII	3	8	9.60	88.27	11.58
30 grams of ether-soluble sol rubber (Pummerer's method)					
VIII	4	3	9.60	...	...
IX	4	7	9.20	88.19	11.67

8 grams of ether-insoluble gel rubber (Pummerer's method).
Total amount decomposed: 38 grams; 2 grams lost in precipitating the fractions.
Extraction agent: I–VII ether, VIII and IX benzene.

After drying in high vacuo the fractions were soluble in benzene and in tetralin. The viscosity increased in the first three fractions in the expected way, then diminished rapidly in the later fractions. Fractions VI–IX showed about the same viscosity.

The result at first was astonishing. Here, too, since an atmosphere of carbon dioxide was used, no explanation could be offered for the decomposition.

Leupold[20] proved by viscosity measurements of balata solutions that even very small quantities of oxygen which are present in the solvent are able to produce considerable decomposition. We found the same sensitivity to the oxygen present in the solvent.

In the first fraction this decomposition was still not very large because here less solvent was used than in the later fractions. Possibly light also causes decomposition.[21]

Fractionation of Rubber in the Cold in Darkness with Complete Exclusion of Air

The three extractions made previously did not give the result which was expected, *i. e.*, that the more difficultly soluble portion would yield higher viscous solutions than the more easily soluble solution. In all cases we attributed the failure to a decomposition of the rubber during the extraction. In the following experiment it was proved that rubber behaved in fractional extraction like polystyrene, *i. e.*, that the most difficultly soluble fraction has the highest molecular weight. For this it is, however, necessary to exclude everything which induces decomposition. Fractionation must therefore be carried out in the dark, and with the most careful exclusion of atmospheric oxygen.

For this reason the solvent was distilled in pure nitrogen, and all operations were carried out in nitrogen. To purify the rubber it was treated with alkali and extracted with acetone, and in order to exclude air and to avoid heating the rubber, the apparatus described by Pummerer[22] for the fractionation of rubber was used.

In this case, also, fractionation of the rubber was carried out in the cold. The entire apparatus had ground glass connections, and, in addition, the solvent was forced out of the lower flask into the upper one by nitrogen, without coming in contact with air. The cooling of the solvent, the concentration of the solution *in vacuo*, and the isolation of the rubber, which was accomplished by pouring the concentrated solutions into methyl alcohol, were carried out in nitrogen. To make the apparatus rigid, glass spirals were fused in at appropriate places. Here also four fractions were prepared by extraction with ether. By extraction with benzene two additional fractions were obtained. In this case 26 per cent of the rubber remained undissolved. This constituted an insoluble rubber which was not even soluble in a great excess of tetralin. This rubber had a somewhat lower carbon content than

TABLE VI

Fractions	Grams	Time of Extraction (Days)	Solubility in Tetralin	Colors	η_r in 0.2-Base Molar Solution (Tetralin) at About 10 Cm. Hg	η_r in 0.2-Base Molar Solution (Tetralin) at About 60 Cm. Hg	Analyses % C	Analyses % C	Analyses % H	Analyses % H
Unfractionated	50	...	Not wholly	Light brown	...	...	88.08	88.20	12.01	11.83
I	5	1	Easily	Almost colorless	4.60	4.20	87.97	88.16	11.77	11.88
II	7	4	Easily		10.42	8.19	88.15	88.09	11.80	11.82
III	8	8	Easily		10.37	8.29	88.09	88.05	11.93	11.90
IV	4	11	Difficultly		14.89	11.07	88.08	88.16	12.00	12.00
24 g. of ether-soluble sol rubber (Pummerer's method)										
V	2	2	Easily	Brown[a]	2.87	2.84	86.06	86.03	11.46	11.35
VI	5	5	Very difficultly	Almost colorless	23.92	16.05	88.26	88.30	12.09	11.73
VII	13	5	Not soluble	Brown	...	...	87.20	87.31	11.61	12.05

20 g. of ether-insoluble gel rubber (by Pummerer's method).
Total amount decomposed 44 g.; 6 g. lost during precipitation of the fractions.
Extraction agent: I–IV ether, V–VII benzene.
[a] Decomposed by oxidation since the glass in which the fraction was sealed had a leak.

the other fractions (see Table VI). In Fractions I to VI, the viscosity increased in the expected way. The difficultly soluble fraction was by far the most highly viscous, therefore the highest molecular. Only Fraction V showed a great anomaly, but in this case the pure substance had been kept in a sealed vessel which had a crack so that air came in contact with this fraction. In this way a considerable

decomposition took place, and therefore Fraction V shows the enormous sensitivity of this pure rubber toward oxygen.

To determine the molecular weight of the fraction, the viscosity of a 0.02-base molar solution in tetralin was measured in the Ostwald viscosimeter at 20° (see Table VII).

TABLE VII

Fractions	Solubility	η_r	η_{sp}	$\frac{\eta_{sp}}{c}$	$M = \frac{\eta_{sp}}{c \times K_m}$ $K_m(3 \times 10^{-4})$	Degree of Polymerization
I	Soluble in ether	1.26	0.26	13.0	43,000	650
II		1.43	0.43	21.5	72,000	1000
III		1.43	0.43	21.5	72,000	1000
IV		1.62	0.62	31.0	103,000	1500
V	Soluble in benzene	1.15	0.15	7.5	25,000	350[23]
VI		2.36	1.36	68.0	227,000	3000
VII	Insoluble	In a 0.02-base molar solution is also insoluble				

Changes in Rubber Fractions on Keeping

The rubber fractions of different average molecular weights were kept in absolute vacuum for a month with complete exclusion of light, and the viscosities of their solutions were determined from time to time. The viscosity of the lowest molecular rubber did not change, that of the higher molecular rubbers, especially of the highest fraction, diminished considerably. We attributed this to the fact that the rubber came in contact with air each time the weighing glass was opened.

TABLE VIII

CHANGE IN RUBBER ON KEEPING. η_{sp} IN 0.2-BASE MOLAR TETRALIN SOLUTION AT 60 CM. Hg PRESSURE

Fractions	Molecular Weight	η_{sp} Immediately after Constant Weight	η_{sp} After Weeks				
			5	8	10	12	20
I	40,000	3.20	...	..	..	3.18	3.18
III	70,000	7.29	7.25	6.57	..	5.95	5.62
IV	100,000	10.07	8.48	8.35	7.32	6.92	7.42
VI	225,000	15.05	12.60	9.79	7.21	Wholly	insoluble

After standing for six months, all the fractions changed more or less completely to insoluble rubber. The transition from soluble to insoluble rubber was quickest with the highest molecular Fraction VI, in fact this took place after only three months. After six months Fraction IV became insoluble; after nine months Fractions I and III. These insoluble rubbers swelled greatly on treatment with solvent without dissolving on long standing and agitating as long as air was excluded. Even with a large volume of solvent only swelling took place and no solution.

In order to dissolve these insoluble rubbers and thus to bring about their degradation, they were shaken with tetralin to which chloroacetic acid was added in the ratio of 0.01 mol per isoprene residue. After one day's shaking with this dilute chloroacetic acid solution, the insoluble rubber was completely dissolved. Heating with tetralin at 60° in the presence of air also resulted in solution. Here the degradation to soluble rubber required a longer time, *i. e.*, it took place in one to two weeks. In all cases enough tetralin was used so that after solution the rubber solutions were 0.2-base molar. The rubber solutions thus obtained were of low viscosity. The degraded rubbers had an average molecular weight of 15,000 to 20,000, and a degree of polymerization of about 200, as shown in the following Table IX.

TABLE IX

Fractions	η_r at 60 Cm. Pressure	Molecular Weight	Number of Months Kept	Decomposition of Insoluble Rubber With Chloroacetic Acid: η_r	Decomposition of Insoluble Rubber With Chloroacetic Acid: Average Mol. Wt. Calcd. from K_e	Decomposition of Insoluble Rubber In Light in Tetralin: η_r	Decomposition of Insoluble Rubber In Light in Tetralin: Average Mol. Wt. Calcd. from K_e
I	4.20	43,000	9	2.07		2.30	18,000
III	8.19	72,000	9	2.14	About 15,000	1.98	15,000
IV	8.20	100,000	6	2.02		2.16	16,000
VI	11.07	227,000	3	2.10		2.25	18,000

Even on long standing in air, the insoluble rubber was converted into soluble rubber, which then yielded solutions of low viscosity; η_r in 0.2-base molar tetralin solution at 20° was 2.20, and the average molecular weight was about 17,000.

The carrying out of this and the preceding work was made possible by the kind assistance of the directors of the I. G. Farbenindustrie-Werk, Leverkusen, to whom we wish to express our thanks at this time.

References

[1] *Kautschuk*, **1928**, p. 97.

[2] Staudinger and Joseph, *Ber.*, **63**, 2888 (1930).

[3] See note 1.

[4] *Kolloid-Z. Zsigmondy-Festchrift*, **1925**, p. 15; Hauser, "Latex," published by Steinkopff, **1928**.

[5] Caspari, *J. Soc. Chem. Ind.*, **32**, 1040 (1913).

[6] Staudinger and Bondy, *Ber.*, **63**, 724 (1930).

[7] Staudinger and Schweitzer, *Ibid.*, **63**, 3154 (1930).

[8] Foll (see *Kolloid-Z.*, **12**, 145 (1913)) has observed that the easily soluble parts of rubber have a lower viscosity than the more difficultly soluble. Also see van Rossem, *Kolloidchem. Beihefte*, **10**, 105 (1919). For experiments explaining these phenomena, see the works of Foll.

[9] *Ber.*, **59**, 3019 (1926).

[10] According to experiments by Heuer. See also Staudinger, Brunner, Frey, Garbsch, Signer, and Wehrli, *Ber.*, **62**, 241 (1929).

[11] Staudinger and Heuer, *Ibid.*, **63**, 222 (1930).

[12] Staudinger and Bondy, *Ibid.*, **63**, 724 (1930).

[13] *Ber.*, **61**, 1583 (1928).

[14] *Ber.*, **60**, 2167 (1927).

[15] Staudinger and Bondy, *Ibid.*, **63**, 2900 (1930).

[16] This instability of bromobenzene is very surprising, and it still remains to be ascertained whether or not impurities act catalytically.

[17] Staudinger and Joseph, *Ber.*, **63**, 2888 (1930).

[18] Staudinger and Machemer, *Ibid.*, **62**, 2932 (1929).

[19] Benzene would be the best extraction agent, but because of its high melting point decomposition might ensue.

[20] Staudinger and Leupold, *Ber.*, **63**, 730 (1930).

[21] For the influence of light on the viscosity of rubber solutions, see van Rossem, *Kolloidchem. Beihefte*, **10**, 109. Earlier investigations on the decomposition of rubber solutions in light were not done with the most careful exclusion of oxygen. These observations are to be explained on the basis that light encourages autoöxidation.

[22] *Ber.*, **61**, 1585 (1928).

[23] Highly decomposed.

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Modifications of the Gutta-Percha Hydrocarbon

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In the past year, a paper was published[1] to show the manner in which the gutta-percha hydrocarbon is altered by fusion. Though the original substance is only slightly soluble in benzene below 19° C. and in petroleum ether (b. p. 50–80°) below 28°, the fused product after resolidification is for the greater part soluble in these solvents at lower temperatures than those mentioned. The solidified product therefore contains one or more new modifications of the hydrocarbon, which are soluble in benzene and in petroleum ether at the lower temperatures. If the petroleum ether solution is allowed to stand at ordinary temperature, a precipitate is formed. Though this precipitate is insoluble in petroleum ether at room temperature, it is in most cases all soluble, and frequently is completely soluble, in benzene below 19°. This modification of the hydrocarbon has the peculiarity, in common with the original substance, that after slight pressing, it is only slightly soluble in benzene below 19°. When a benzene solution of the uncompressed precipitate is allowed to evaporate slowly at ordinary temperature, there is obtained a film which is likewise only slightly soluble in benzene below 19°.

By x-ray examination, Hopff and von Susich[2] have found that a stable or α-modification passes on fusion into an amorphous form, which on cooling changes to a metastable β-modification.

In view of these facts, it was necessary to ascertain to what extent the observed differences in solubility of the products obtained from the fused hydrocarbon might be explained by the three modifications found by Hopff and von Susich. J. R. Katz has undertaken the x-ray investigations necessary to this end, and the results obtained up to this time on the problem are described below.

The film obtained by the slow evaporation of a benzene solution at ordinary temperature, which is the stable modification, showed the x-ray diagram of the α-form, in agreement with Hopff and von Susich.

The precipitate which settles out when the petroleum ether solution is allowed to stand could also be easily obtained by dissolving the α-form in hot petroleum ether and allowing the concentrated solution to crystallize. In most cases a very voluminous mass was obtained, which filled the solution like a sponge. In many cases it dissolved easily in benzene below 19°, both when damp and after drying in air, as long as pressing was avoided.

When the air-dried product was placed in benzene below 19°, it became transparent and numerous small air bubbles, indicative of its spongy character, were visible.

When sealed in a thin-walled capillary tube, this spongy product gave either in petroleum ether or in the dry state (when care was taken to avoid pressing) the x-ray diagram of the α-form. After exposure to x-rays, the dry product was easily soluble in benzene below 19°, so that it had not been altered by the exposure. The product, obtained by compressing the spongy mass, also gave the x-ray diagram of the α-form, and its solubility was the same.

The effect of the pressing was also visible in a small piece cut from the dry product. A thin strip which was compressed by the action of scissors had not disappeared after one day in benzene, whereas the uncut part of the sample dissolved completely in a few minutes.

When the spongy product was compressed on a microscopic slide, it became a transparent mass. In parallel polarized light between crossed nicol prisms, it remained dark. When it was rubbed in a definite direction, there was immediate extinction, indicating that this action causes an orientation of the crystals.

When the spongy product was only partially dissolved in hot petroleum ether and was then allowed to recrystallize, and this operation was repeated several times, a change took place. The product was then only partially soluble in benzene below 19°. Microscopic examination (70 times) showed separate tiny needles in the mass, which were particularly visible as luminous little streaks or points when viewed in rectilinear polarized light between crossed nicol prisms. These showed straight extinction. In the part of the product which was insoluble in benzene below 19°, numerous small and a few large needles were visible, and perhaps the insoluble product consisted wholly of these needles. The residue which remained undissolved, when the already modified product was dissolved in hot petroleum ether, also showed small needles. It is not improbable that the difference between the solubility of the spongy product and that of the compressed product depended merely upon an impurity.

Since, as has already been observed,[3] the hydrocarbon of sheet balata is less impure than that obtained by extraction from old leaves, a spongy product was also prepared from sheet balata by solution in petroleum ether and crystallization of this solution at 15°. It was removed, was washed with petroleum ether, was dissolved in this solvent, fuller's earth was added, and the solution was filtered. On the following day the sponge separated as a colorless product. It was again removed, washed, once more recrystallized from petroleum ether, and left in darkness for one day to free it of petroleum ether.

Upon agitation with benzene, the following results were obtained with this product:

1.407 grams were shaken with 125 cc. of benzene. 1.421 grams which had previously been compressed in a mortar to 44 little flat pieces were also shaken with 125 cc. of benzene. After a definite time, about 20 cc. were removed and filtered. The filtrate and the residue after distillation were weighed. The following quantities (in mg.) were obtained from 10 g. of filtrate:

	Immediately after Addition of Benzene	After 0.5 Hour	After 1 Hour	After 1.5 Hours	After 2 Hours
Temperature	16.5°	16.75°	17°	17.25°	17.5°
Not compressed	13	23	41	121	20
Compressed	1	7	7	7	12

It is evident that during the shaking more and more of the uncompressed substance dissolved, until after 2 hours' agitation the greater part of the dissolved part had again separated. After standing for 24 hours the quantity in the filtrate (17 mg. at 17°) was not very different from that from the compressed substance (16 mg. at 17°).

The rest of the spongy product was then left in contact with benzene for 24 hours at 16.5°, was then removed, washed with benzene, and left exposed to the air in darkness for one day.

1.851 grams of this product were agitated with 125 cc. of benzene, and filtered. Ten grams of the filtrate gave the following yields (in mg.):

	After 0.5 Hour	After 1.5 (?) Hours	After 2.5 Hours
Temperature	15.5°	15.75°	16°
Not compressed	1.5	3	6

The filtrate obtained after 24 hours' standing contained only 6 mg. in 10 grams. The properties of this purified product will be described in a later paper.

A few tentative experiments were also carried out to determine the influence of extraction of the resolidified fused hydrocarbon with benzene and with petroleum ether. Thin strips were used for the determinations, and they were kept in benzene for 24 hours at a temperature below 19°. The solution was then poured off, more benzene was added to the residue, and after 24 hours the new solution was again removed. The solutions thus obtained were distilled, the flasks were blown out, and were weighed after 1 hour.

In the extraction with petroleum ether (b. p. 50°–80°), the solution was poured off after 1 hour, because after 1 day it had for the most part already crystallized. The petroleum ether added afterward was removed on the following day.

The values obtained do not give a definite clue to the composition of the fused hydrocarbon, because it is possible that the thickness of the strips had an influence on the results. Moreover, the experiments to be described show that by extraction with benzene the easily soluble modification or the modifications concerned may be converted into the α-form.

The strips were fused in water at 100° and slowly cooled by allowing the water to cool. They gave a mixed x-ray diagram characteristic of a mixture of the β- and α- forms; 146 mg. lost 76 mg., *i. e.*, 52 per cent in benzene at 16°. The insoluble part gave the x-ray diagram of the α-form. Since the α-interference circles of the original strips were weaker than they would be if they consisted of 50 per cent of the α-form, the extraction with benzene must have resulted in a partial transformation of the β-form into the α-form.

Strips which had been fused at 100° and cooled rapidly in a current of water, gave the x-ray diagram of the β-form. 141 mg. lost 103 mg., *i. e.*, 73 per cent in benzene at 16°. Here, too, the residue gave the x-ray diagram of the α-form, and therefore the β-form had been converted into the α-form. A second experiment gave a similar result.

Since Hopff and von Susich have reported that heated samples have a strong tendency to remain amorphous for a long time, benzene may have dissolved not only the β-form but also the amorphous form, and the latter, or both the latter and the β-form, may have been transformed into the α-form.

A few strips were fused at 100° and cooled on ice, as a result of which they gave the x-ray diagram of the β-form. From 123 mg., 49 mg. were extracted by petroleum ether at 21°, *i. e.*, 40 per cent. The residue gave the x-ray diagram of the β-form. A second experiment gave a similar result.

Petroleum ether dissolves the amorphous form and also part of the β-form, but it does not transform the β-form into the α-form.

A few experiments were also carried out to learn the influence of compression (by means of a hand press) on the solubility of fused strips in benzene at 16°. It resulted that 193 mg. of slowly cooled product lost 54 mg., *i. e.*, 28 per cent, whereas 229 mg. of the same product cold-pressed lost 28 mg., *i. e.*, 12.5 per cent; 249 mg. of rapidly cooled product lost 137 mg., *i. e.*, 55 per cent, and 192 mg. of the same product cold-pressed lost 29 mg., *i. e.*, 15 per cent.

Consequently, as found with the spongy product, compression diminishes the solubility of strips in benzene at 16°, in spite of the increased surface area. Since it is probable that there is also a pressure exerted when strips are stretched in the cold,

strips which had been fused in a calcium chloride bath at 120° and quenched in water at 18° were stretched in the cold. Unstretched, 145 mg. lost 73 mg., *i. e.*, 50 per cent, whereas 154 mg., previously stretched from 11 cm. to 22.3 cm. while cold, lost 23 mg., *i. e.*, only 15 per cent.

The original strips gave the x-ray diagram of the β-form, while that of the stretched product was oriented. After treatment with benzene they gave the x-ray diagram of the α-form, and again the stretched product was oriented.

The total surface area of the stretched strips was about twice that of the unstretched strips.

The stretching of cold threads which had been prepared from the fused hydrocarbon had only a slight influence on their solubility in benzene, as seen from the following results.

Two threads, 95 cm. and 157 cm. long, were divided in equal parts, and a part of each was stretched until the two halves reached lengths of 73 cm. and 131 cm., respectively. The unstretched part at 11° lost 39 per cent, and the stretched part also lost 39 per cent. The surface of the stretched part was about 1.5 times as great as that of the unstretched part, so that the unstretched part lost more per unit surface area than did the stretched part.

These investigations are to be continued with material purified by benzene.

Summary

The spongy product from gutta-percha hydrocarbon, which is obtained from a concentrated petroleum ether solution, consists of microcrystals of the α-modification. The difference in its solubility and that of the compressed product prepared from the spongy product is perhaps attributable to the presence of an impurity.

By treatment of the fused hydrocarbon with benzene below 19° C. both the β-form and the amorphous form dissolve, and one of these forms is converted, or perhaps both of the forms are converted, into the α-form. It is possible that petroleum ether dissolves not only the amorphous form but also a part of the β-form. It does not, however, transform the β-form into the α-form.

Compression in the cold of previously fused strips, as well as of strips elongated while cold, decreases the solubility of these strips in benzene below 19° C.

Cold-drawing of threads, which have been prepared from fused products, has only a slight influence on the stability of the threads in benzene below 19° C.

References

[1] *Rec. trav. chim.*, **49**, 827 (1930).
[2] *Kautschuk*, Nov., **1930**.
[3] *Rec. trav. chim.*, **50**, 1018 (1931).

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The Reënforcement of Rubber

G. Antonoff

It is a well-known fact that, when mixed in rubber, certain powders reënforce the latter to a considerable extent, whereas others have no effect or only a relatively slight one.

Since the nature of the phenomena which take place under these conditions in rubber is far from well established in the present state of knowledge, I have carried out certain experiments of a very simple kind which will by analogy throw some light on the subject.

I have found that very important information can be obtained from the study of some physical properties of mixtures of different powders in organic liquids. For a beginning, ordinary paints were tested, but the presence of drying oils complicated matters and it was found advantageous to replace the linseed oil with a non-oxidizing oil, as for example, peanut oil. In this way, pastes of different concentrations were prepared, and the resistance to rupture of the films of these pastes was measured by a method often used to determine the surface tension of liquids. A convenient method of operation is as follows: two thin rods are wet with the paste and are made to adhere to one another. The upper rod A is fastened permanently in a way not shown in Fig. 1. From rod B hangs a pan for small weights which, added in convenient quantity, will finally bring about rupture of the film and separation of the two rods.

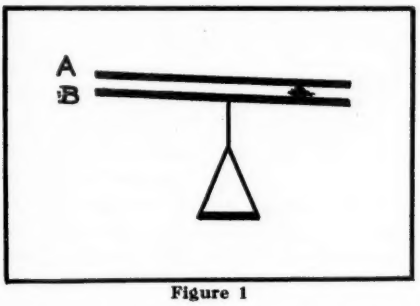


Figure 1

The load at rupture per unit length or the surface tension of the film of paste is obtained by the formula:

$$\alpha = \frac{P}{2l}$$

where α is the surface tension of the film, P the weight applied, and l the length of the rod.

Expressed as usual in dynes per centimeter, the surface tension of the oils is of the order of magnitude of 30 to 40 dynes per centimeter.

Pastes can be used in these experiments even when they have considerable viscosity. It should be mentioned here that the tension at rupture bears no relation to the viscosity; the viscous film may sometimes have a very low resistance to rupture and *vice versa*. Since the temperature coefficient of viscosity is enormous, *e. g.*, 25 per cent, the mass may become far less viscous when the temperature is raised, and yet this has only a very slight effect on the load at rupture.

In preparing pastes with different powders it was proved that some of them cause a considerable reënforcement, *e. g.*, the tension at rupture may be from 800 to 1000 dynes per centimeter, or even more, whereas certain others produce absolutely no effect, the surface tension of the paste being practically equal to that of the oil.

It is evident, therefore, that there is a substantial difference in the nature of the two kinds of pastes.

In fact, pastes of the second type, of which many are made by mechanical grinding, show a layer of pure oil on their surface if they are left standing for some time. When used as paint, they will always give a homogeneous surface because of the fact that the oil film comes to the surface upon standing, even if they are very viscous. Such paints sometimes have advantages.

On the contrary, with pastes of the first type in which there is reënforcement, there seems to be no separation at all. There is an intimate association between the particles of paint and the liquid which renders them inseparable by mechanical means and which must be the result of a field of force formed by contact of the paint and the oil. In this case the liquid probably carries an electric charge of a certain sign and the particles of pigment the contrary sign, so that their intimate mixture brings about the formation of a sort of electric doublet. The moment of this doublet depends upon the previous history of the pigment. In my experi-

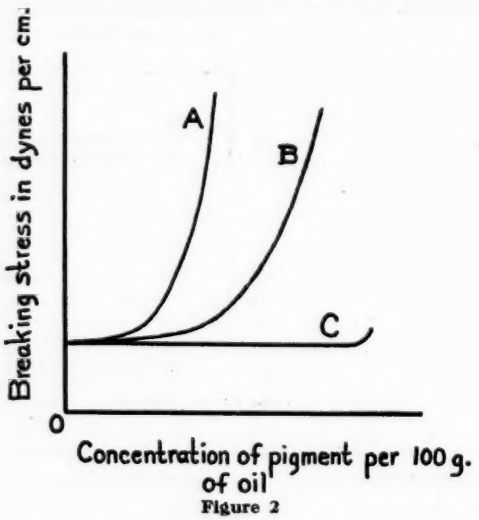


Figure 2

ments of the present work, cases were found where particles of the same substance showed a high reënforcing power, whereas prepared in a slightly different way the same substance had totally different properties and it no longer reënforced the oil. Probably, as a result of a different configuration of the particles, the electric moment became 0 or almost 0, and such a substance became indifferent with respect to the liquid.

Measurements of the breaking strength as a function of the concentration of the paste gave curves like those of Fig. 2.

Each of the curves was obtained with a different powder. In every case, the powder was mixed with the oil by rubbing it with a spatula, after which portions of the paste were diluted with increasing quantities of oil.

The paste which received the longest mechanical treatment gave the most rapidly ascending curve.

By subjecting the paste to prolonged mechanical treatment, the curve has a more rapid ascent.

Thus, for a given substance ground to different degrees, the curves are a *measure of the fineness of the powder*.

In the case of a curve like C in Fig. 2, mechanical grinding produces no effect.

It was then of interest to try to find out what other properties are related to the general character of the curves.

In this connection it will perhaps be interesting to recall certain facts. For example preliminary experiments with this method have been described by the author in two publications (*e. g.*, *Phil. Mag.*, June, 1926, page 1263, and October, 1927, page 792), and in one an example of a highly reënforced curve is that obtained with mixtures of lamp black and oil.

Some time after this publication I received a letter from an American author telling me that he had attempted to reproduce my experiments with different kinds of carbon, but he had been able neither to obtain the same nor similar results.

Having prepared some carbon blacks by carbonization of carboniferous substances and having divided them as finely as possible by mechanical means, the same result was again obtained, *viz.*, carbon black does not reënforce, the curve obtained being like that of C (Fig. 2).

Following this, a number of carbons in a state of extreme fineness were prepared by various chemical processes, and it was proved that some of them had a great reënforcing effect, in fact much greater than that of lamp black, and of the best grades of carbon black. Figure 2 shows that the greater the reënforcing effect of the product, the more displaced to the left is the more rapidly ascending part of the curve.

These carbons were likewise found to reënforce rubber, whereas the various kinds like that represented by curve C did not act in this way.

From this point of view it is of interest to recall the work of Esch (*Gummi-Z.*, **42**, 1921 (1928)) who found that the ratio between the apparent density Δ (weight of a unit volume of powder) and the true density δ, *e. g.*, the density determined by a densimeter in a liquid,

$$\frac{\Delta}{\delta},$$

varies almost inversely with the reënforcing power in the rubber. According to this author, this ratio is a measure of the degree of fineness.

Whether this is exact or not, the general evidence indicates that, starting with certain values of Δ or of $\frac{\Delta}{\delta}$ in decreasing order, the forces of cohesion become manifest and at the same time exert an appreciable influence on the pastes and on the rubber mixtures.

All the same, this does not mean that Δ or $\frac{\Delta}{\delta}$ is the measure of the degree of fineness.

Among carbons prepared in the present work, the apparent density Δ varied within the limits 0.6 and 0.08, the corresponding values of $\frac{\Delta}{\delta}$ from 0.4 to 0.02; the values for lamp black and carbon black were 0.09 to 0.06.

On the whole, I found the more voluminous the powder the greater was the reënforcing effect. In the case of carbons, the phenomenon is complicated by the fact that the true specific gravity varies with the method of preparation of the product.

It is not certain whether Δ or $\frac{\Delta}{\delta}$ is to be preferred as a measure of the reënforcing power, because they both change more or less in the same order, and they seem satisfactory for practical needs.

In other cases, such as iron oxide, a great many products were prepared, but their true density δ remained constant. In these cases, the apparent density Δ is a measure of the reënforcing power.

Résumé

In paints and in rubber the more voluminous is the filler, the greater is its reenforcing power. This does not mean that the voluminosity is a measure of the fineness, but it is closely related to the formation of intense cohesive forces, and these are the cause of the reënforcing action.

[Translated from Revue Générale du Caoutchouc, Vol. 8, No. 75, page 19, October, 1931.]

The Minimum of Sulfur Required for Vulcanization

A Résumé

G. Bruni

The problem of the minimum proportion of sulfur necessary to effect vulcanization is fundamental to an interpretation of the very nature of vulcanization itself.

Since the introduction of ultra-accelerators, it has been recognized that very small quantities of sulfur are sufficient to bring about vulcanization.

In experiments carried out in 1918 in collaboration with G. Menghi in the Laboratory of Chemical and Physical-Chemical Research of the Pirelli Company of Milan, the author found that by the aid of zinc dimethyldithiocarbamate or of similar substances there is an appreciable vulcanization with 0.2 per cent of sulfur. This fact was made public in patents applied for by the author the next year.

On the other hand, it is generally recognized today that all vulcanization originates in a chemical reaction, though a fundamental difficulty lies in the fact that it has never been possible to give an exact definition of what is meant by vulcanization. When is a rubber considered vulcanized? From a technical point of view this question may be answered, but there has not been a satisfactory explanation up to this time.

In so far as vulcanization by sulfur alone is concerned, the question may be put as follows: If certain physical properties of rubber mixtures, which are identical except for increasing proportions of sulfur and which have received the same thermal treatment, are measured and a diagram is constructed showing these properties as a function of the percentage of sulfur, will a continuous curve be obtained or will it be possible to identify a critical point which can be regarded as the onset of vulcanization? In other words, can the minimum of sulfur necessary for vulcanization be established, and if so how great is this minimum?

The author has undertaken several parallel series of experiments which were carried out by Dr. Oberto of the Physical Laboratory of the Pirelli Company of Milan to try to clear up this point.

The rubber mixtures which were used contained 100 parts of first latex crepe, 5 parts of zinc oxide, variable proportions of an ultra-accelerator (0.5, 1.0, and 1.5 per cent of piperidyl pentamethylenedithiocarbamate), and for each of these three series, proportions of sulfur from 0.1 to 1.0 per cent.

Each series was vulcanized at 100° for periods varying from 10 to 60 minutes. After vulcanization tests were made on a Schopper dynamometer.

With the sulfur contents as abscissa and with the loads (in grams per millimeter of original cross-section) at 600, 700, and 800 per cent elongation as ordinate, each series gave curves which were straight lines.

When extrapolated, these straight lines converged and cut the abscissa at practically the same point, *viz.*, at 0.15 per cent sulfur, based on the rubber.

It therefore seems reasonable to consider that this proportion corresponds very closely to the minimum of sulfur required for the beginning of vulcanization, and this corresponds in turn to about one atom of sulfur per 310 isoprene C_5H_8 radicals.

From this result, theoretical conclusions on the phenomenon of vulcanization and on the constitution of vulcanized rubber will be drawn later.

[Translated from Revue Générale du Caoutchouc, Vol. 9, No. 79, pages 5–9, February–March, 1932.]

Remarks on the Formation of Jellies in Rubber Solutions Containing Ultra-accelerators

Influence of the Solvent

R. Thiollet

Rubber solutions are used for coating fabrics, for cementing pieces of rubber, and for manufacturing certain objects like nipples. These various articles can be vulcanized in the cold with sulfur chloride, but it is becoming more and more popular to vulcanize them by the hot method, which necessitates the use of ultra-accelerators.

Rubber solutions containing ultra-accelerators are often transformed, in some cases rapidly, into jellies which are absolutely useless. In connection with the formation of these jellies, we have made certain observations, which it is believed will be useful in the preparation of solutions containing these rapid accelerators.

These observations deal with: (1) the influence of the accelerator, and (2) the influence of the solvent, on the rapidity of the formation of jellies.

We studied first of all tetramethylthiouram mono- and disulfide, which are the accelerators most often used for vulcanizing in hot air. We have studied them alone and in combination with other accelerators, such as mercaptobenzothiazole, ethylidene-aniline, and anhydroformaldehyde-aniline.

The solutions were made under the following conditions. A series of mixtures containing different accelerators was prepared from the same base mix by mixing on a roll mill. These mixtures were prepared with a constant distance between the rolls, and by passing the mixtures through the same number of times.

Aliquot parts of the mixtures were then dissolved separately in benzene, in gasoline, and in trichloroethylene, in the proportion of 1 part of rubber to 10 parts of solvent.

The solutions were agitated slowly for 10 hours, and were let stand 12 hours before the first viscosity measurements were made. The solutions were kept at a temperature of about 25° C. The formation of the jellies was followed by measuring the viscosity from time to time.

Measurements of the viscosity of very thick rubber solutions are not very precise, especially when the moment approaches when the solution is about to become a jelly, but the changes in the values, corresponding to different states of solution, are sufficiently large for the results obtained to be easily interpreted.

First Series of Experiments

The following mixtures were prepared:

	1	2	3
First latex crepe	100	100	100
Zinc oxide	5	5	5
Sulfur	2.25	2.25	2.25
Tetramethylthiouram disulfide	0.4	0.4	0.4
Ethylidene-aniline	1	..	..
Anhydroformaldehyde-aniline	..	1	..

Let B_1, B_2, and B_3 represent the solutions in benzene, G_1, G_2, and G_3 the solutions in gasoline, and T_1, T_2, and T_3 the solutions in trichloroethylene.

Solutions in Benzene

It was proved that the viscosity of these solutions varies appreciably up to the moment of the formation of the jelly. The transformation into a jelly takes place very suddenly, without a progressive increase in viscosity just previous to gelation.

Solution B_1 was transformed into a jelly after 2 days, solution B_2 after 35 days, and solution B_3 after 37 days.

Since anhydroformaldehyde-aniline acts as an "antiscorch" by diminishing the precocity of rapid accelerators, it might be thought that this substance would retard the formation of jellies in rubber solutions containing rapid accelerators. However, the jelly was formed as rapidly in solution B_2 containing anhydroformaldehyde-aniline and tetramethyldithiouram disulfide as in solution B_3, which contained only tetramethylthiouram disulfide.

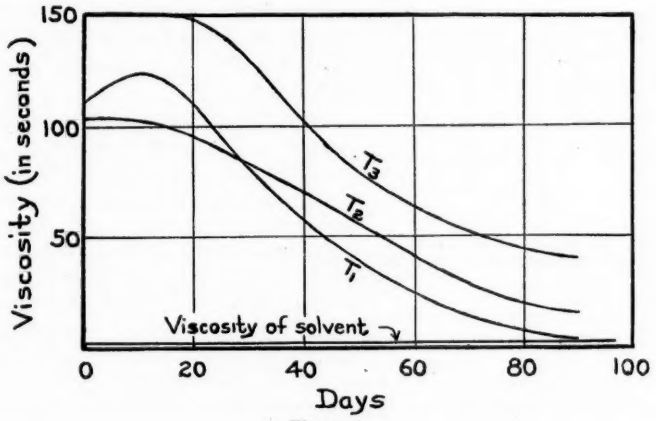


Figure 1

On the other hand, ethylidene-aniline increased considerably the rapidity of the formation of the jelly, since solution B_1 was transformed into a jelly after 2 days.

Solutions in Gasoline

Although the formation of jellies takes place very suddenly in benzene, it takes place very gradually in gasoline. In this latter solvent, the appearance of the jelly is much later than in benzene.

Solution G_1 formed a jelly after 18 days, in contrast to 2 days for solution B_1.

After 90 days, solutions G_2 and G_3 had become very viscous, but even then had not become completely transformed into a jelly.

Gasoline solutions of mixtures containing rapid accelerators also had less tendency to gel than those with benzene.

Solutions in Trichloroethylene

The formation of jellies in solutions of trichloroethylene was never observed. Figure 1 shows the way in which solutions T_1, T_2, and T_3 varied.

The time of flow of the solutions, expressed in seconds, is shown as ordinate, while the number of days of rest of the solution is shown as abscissa.

The curves thus obtained resemble very closely those obtained for solutions containing neither sulfur nor accelerator.

The viscosity of solution T_3 at the beginning of the experiment was distinctly greater than the viscosities of solutions T_1 and T_2. A comparison of the variations in the viscosities of these last two solutions alone showed that at the moment of preparing the solutions the viscosities were very similar. The viscosity of T_1 increased at first a little, probably because of the action of the accelerator, then it diminished. That of T_2 remained constant for several days at first, and then diminished. At the end of the experiment, that is, after 90 days, the viscosity of solution T_2 was much greater than that of solution T_1, in fact the former corresponded to a time of flow of 15 seconds, while the latter corresponded to a time of flow of 3 seconds.

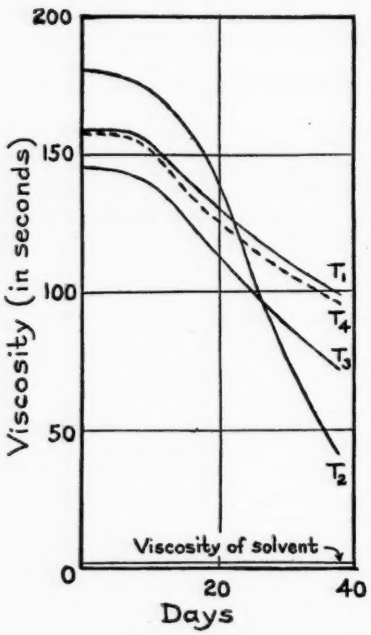


Figure 2

Since the viscosity of the solvent corresponded to 2 seconds, solution T_1 was close to its limiting viscosity after 90 days.

It must be mentioned that viscosity measurements carried out on solutions which are more fluid than at the moment of their preparation become much more precise, and the values can then be accepted without great danger of error. Moreover, with trichloroethylene the measurements were relatively easy throughout the experiment.

Solution T_1, containing the most active accelerator, had after 90 days the lowest viscosity.

Second Series of Experiments

The following mixtures were prepared:

	1	2	3	4
First latex crepe	100	100	100	100
Zinc oxide	5	5	5	5
Sulfur	2.25	2.25	2.25	2.25
Mercaptobenzothiazole	1	..	0.5	..
Tetramethylthiouram-monosulfide	..	0.5	0.25	..

Let B_1 B_2 B_3 B_4
G_1 G_2 G_3 G_4
T_1 T_2 T_3 T_4

represent the solutions of the mixtures in benzene, in gasoline, and in trichloroethylene, respectively.

After 38 days' rest, none of the solutions had changed to a jelly. It was proved, as in the first series of experiments, that the viscosity of solutions containing the most active accelerators diminished most rapidly. Fig. 2 shows that solution T_2 had after 38 days the lowest viscosity.

When coatings prepared with the different solutions were vulcanized in hot air, and when the time of cure was prolonged beyond the maximum time for vulcanization, the samples made from solutions B_2, G_2, and T_2 became sticky much more rapidly than the others. On the other hand, the viscosities of the solutions B_2, G_2, and T_2 diminished the most rapidly.

It seems, therefore, that from the moment that the viscosity begins to diminish, the accelerator not only no longer accelerates the vulcanization of rubber, but it accelerates its degradation.

This is an action which is comparable to that of the reversion of vulcanization in the presence of rapid accelerators. If the time of heating a mixture containing a rapid accelerator is prolonged, the physical properties first increase, then decrease. The mixture becomes soft; it is devulcanized.

It has been our experience that the degrading action of the solvent takes the place of the degrading action of heat. Moreover, after a certain time solutions in trichloroethylene give coatings which can no longer be vulcanized.

Vulcanization Tests

To study vulcanization, the solution was spread on a galvanized iron plate, the solvent was allowed to evaporate, and vulcanization was carried out in hot air at 125° C. The vulcanized film could be easily separated from the metal plate, but it was difficult to determine its tensile strength. This is why the state of cure was estimated only by hand tests.

Vulcanization tests were made 8 days after the preparation of the mixtures. After 30 minutes in the oven at 125° C., only the coatings corresponding to B_2 and B_3 were cured. After 45 minutes coatings corresponding to B_1, G_1, and T_1 were distinctly undercured, whereas B_2 and B_3 were very well cured. T_2 and T_3 were cured much less than the preceding ones. G_2 and G_3 were in a state of cure intermediate between the samples corresponding to B_2 and B_3 on the one hand and T_2 and T_3 on the other. Consequently the solvent, probably as a result of its degrading action on the rubber in solution, influenced the rate of vulcanization of the coating.

Choice of Solvent

Each solvent, therefore, is of particular interest. Solutions in trichloroethylene do not form a jelly, but give coatings which are more difficult to vulcanize than those prepared with benzene or gasoline. At the end of a certain time the solutions give coatings which can no longer be vulcanized. With trichloroethylene, it is possible to prepare self-vulcanizing solutions, where all the ingredients are dissolved and are not merely in suspension, which assures a perfect homogeneity throughout the mass. In fact, trichloroethylene is an excellent solvent of organic accelerators such as thiouram derivatives, aldehyde-amine condensation products, and dithiocarbamates of amines.

It is an equally good solvent for sulfur. The latter dissolves very easily in hot trichloroethylene. Even when cold the solubility of sulfur is 25 grams per liter of solvent. Of course sulfur dissolves only if it is crystallized. If the only available sulfur is amorphous sulfur, which is insoluble in all solvents, heating to 120°–130° C. is sufficient to transform it into sulfur that is soluble, particularly in trichloroethylene.

To promote the action of the accelerator, a little zinc stearate, which is likewise soluble in trichloroethylene, can be added. Since, however, zinc stearate has a tendency to "bloom," it hinders the adhesion of the fabrics coated with the solu-

tion. It can be replaced by a small proportion of an aldehyde-amine condensation product, which renders certain accelerators active in the absence of zinc oxide.

The disadvantage of these solutions is, as has been seen, the rapid degradation of the rubber they contain. After a relatively short time, which may be only 4 to 8 weeks, especially in summer, the fabrics prepared with these solutions are no longer self-curing or cannot even be vulcanized at all.

With benzene, "nervy" coatings can be obtained, but this is the solvent in which jellies form most rapidly. However, it is easily used since the experiments show that benzene solutions of mixtures containing thiouram derivatives can be kept for more than a month.

Gasoline has a behavior intermediate between that of benzene and of trichloroethylene. Gasoline solutions can be kept for a much longer period than benzene solutions without fear of the formation of a jelly. However, after vulcanization, coatings made from gasoline are less "nervy" than those from benzene.

It seems advantageous to use a mixture of benzene and gasoline. This latter solvent, less volatile than benzene, stabilizes the evaporation and avoids the condensation of the humidity that is sometimes formed on the surfaces of the coatings, as a result of a too rapid evaporation of the solvent.

Trichloroethylene, which is non-inflammable, is an excellent solvent for rubber and a good solvent for sulfur and many accelerators, but it should be used only when the solutions are to be used shortly after their preparation.

[Translated from Revue Générale du Caoutchouc, Vol. 8, No. 71, pages 9–24, May–June, 1931; No. 75, pages 39–54, October, 1931.]

Experiments on the Autoöxidation of Rubber and the Catalytic Phenomena Which Are Associated with It

Charles Dufraisse and Nicolas Drisch

The autoöxidation of rubber has been known for a long time, and for a long time, too, it has been known that it plays an important part in spontaneous deterioration or aging, and it has been the object of numerous studies of much interest.[1,2] Nevertheless, there is little known about the autoöxidation of rubber even now, and the exact part which it plays in aging is still unknown.

In view of this we undertook to apply to this reaction between rubber and free oxygen methods of investigation which one of us has used in collaboration with Charles Moureu for many years in studying the antioxygenic phenomenon.

The aging of rubber is the result of many factors which occur simultaneously or successively. In order to understand this phenomenon, it is necessary to study the various problems separately in so far as possible, and in view of their greater complexity not to consider them all at one time.

With this in mind, we first of all turned our attention to an independent study of autoöxidation by separating it as completely as possible from all interrelated influences, and reserving for a second step in the investigation the reactions of aging itself.

The present work is concerned only with the rate of absorption of oxygen by rubber and the different influences which are capable of modifying it. It deals therefore with the direct measurement of the quantities of oxygen and not with the usual physical tests (elongation, tensile strength, etc.), and we shall be concerned with the physical tests only in our later studies of the relations between oxidation and deterioration.

I. Principle of the Method

Our experimental method was that used by Moureu, Dufraisse, and their collaborators for the study of autoöxidation in general. In principle it consists in enclosing the substance to be tested with oxygen in a glass receptacle of very small capacity and measuring the rate of absorption by the manometric method. In the graphs the abscissae represent the times and the ordinates the heights to which the mercury rises in the manometer after all corrections have been made. Accordingly, the curves actually correspond to the rise of the mercury, but since they follow with few deviations the oxidation curves they are just as well suited for comparisons as are the latter, and since we have only comparisons in view we have adopted them for greater simplicity in the calculations.

Perhaps the question will be raised whether a method adapted to other substances is well suited to a substance as peculiar as rubber, and if rubber does not require special methods of study. This is not important, as will be seen later, because from the point of view of autoöxidation, rubber is not different from other autoöxidizable substances, and therefore the same methods of study are applicable.

A. Incipient Oxidation

There is one point in our technic which we wish to point out, that is, the quantity of oxygen absorbed. In theoretical studies it is customary, just as in technical tests on the oxidation of rubber (Geer oven and Bierer and Davis methods), to use large quantities of oxygen. In our tests, on the contrary, only low proportions of oxygen were used, in general less than 1 per cent, in other words less than 0.02 molecule per molecule of isoprene. In short, we are concerned only with the beginning of oxidation. Surprising as it seems, incipient oxidation is of considerable interest for the following reasons.

1. Autoöxidation is in itself a complex reaction, especially when a substance like rubber is involved which, by coupling, can produce new molecules, themselves autoöxidizable, sometimes with an even greater capacity for self-oxidation than the original molecules. In this way, if the attack by oxygen is carried too far, oxidation of non-rubber molecules takes place, and there is no means of distinguish-

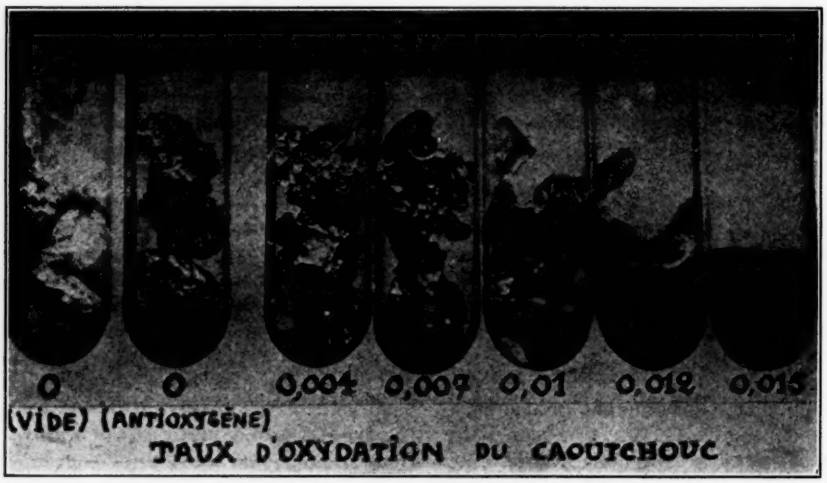


Figure 1—Influence of Very Small Proportions of Oxygen on the Alteration of Raw Crepe Rubber (Extracted with Acetone) When Heated. All These Samples Were Heated for the Same Length of Time (19 Hours at 80° C.), the Only Variation Being the Proportion of Oxygen Previously Absorbed

ing this latter effect in the total oxidation. There is nothing, in fact, to be gained by this information about the behavior of these accessory substances in air, particularly if it involves the risk of complicating any conclusions on the rubber itself.

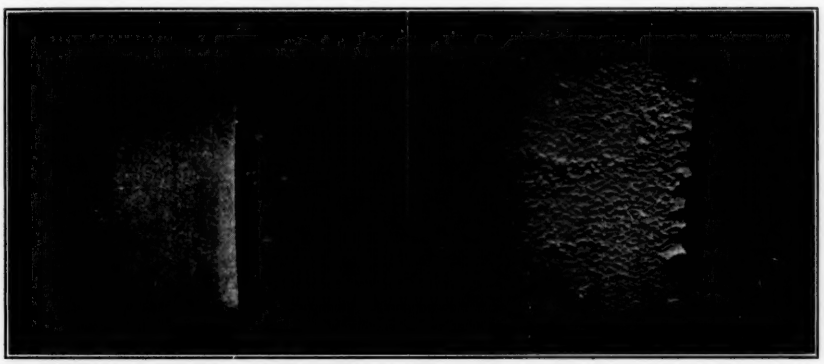
2. The deleterious effect of oxygen is not always evident with large quantities; it may appear with small quantities because it sometimes plays the part of a catalyst. Recently we have described characteristic examples, such as acrolein, CH_2:CHCHO, the first member of the aldehydes with an ethylenic function. When this substance is prepared so that it is completely free of oxygen, it remains perfectly clear in darkness. However, if only the slightest trace of oxygen is introduced, it is not long before the liquid becomes cloudy and gives a precipitate, the volume of which increases until the whole becomes a solid mass, disacryl, which resembles porcelain. The quantity of oxygen which is able to start this transformation is extraordinarily small; we have proved that it is of the order of 1 to 100,000.[3]

Other observations of the same kind have also been made in a similar way on substances more nearly like the present subject, that is, hydrocarbons like styrolene, $C_6H_5CH:CH_2$. The latter is transformed into a vitreous mass, polystyrolene, by quantities of oxygen less than 1 per cent by weight, that is, very small proportions.

Accordingly, in these transformations oxygen has an effect out of proportion to the quantities used. Furthermore, as far as rubber itself and similar substances are concerned, Staudinger[4] has proved in his excellent work the remarkable influence of very small quantities of oxygen.

Therefore, in carrying the oxidation of rubber too far there is danger of obscuring the primary phenomenon by the secondary phenomena, which are more or less a result of the primary phenomenon and which interfere with it.

3. A large proportion of oxygen is not at all necessary to carry rubber to the point where it becomes useless. In all cases much less oxygen is required than that corresponding to the attack of all the ethylene bonds, *i. e.*, one molecule of



0 (vacuum) 0.006

Figure 2—Photomicrographs of Two Samples of Vulcanized Rubber (Elongated 300 Per Cent and Magnified about 10 Times), Showing the Influence of a Small Proportion of Oxygen on the Alteration in the Cold and in Light. The Two Samples, Cut from the Same Sheet (Diphenylguanidine Was the Accelerator Used) Were Therefore Identical. They Received the Same Radiation 4 Days in Sunlight, but the Right Hand One Alone Was Slightly Oxidized

oxygen per one of isoprene. Kohman,[5] among others, has shown that rubber loses one-half its elasticity when it absorbs 0.5 per cent of oxygen by weight, or 0.01 molecule per molecule of isoprene.[6] We ourselves have found that less than 0.004 part of oxygen (based on the raw rubber) or 0.008 molecule per isoprene molecule is sufficient to bring about positive evidence of turning to fat (Fig. 1).

We are equally certain that when vulcanized rubber has absorbed a similar proportion, *i. e.*, 0.006 part or 0.012 molecule per isoprene molecules, under similar conditions, there is already evidence of deterioration (Fig. 2).

We therefore are justified in expecting useful information from our study of incipient oxidation.

B. Technic

We shall not give the details of our technic here, for this is found in publications by Moureu and by Dufraisse, but shall mention only that oxygen was used at a pressure not exceeding 760 mm. On the other hand, it is well to describe the manner of introducing the catalysts into the rubber samples.

Naturally, the ordinary industrial process of mixing was used, but in a systematic study such as ours where a large number of tests were made, it has the disadvantage of being both complicated and less certain for comparisons. On account of its great sensitivity, our technic requires, it is true, as little handling of the samples as possible, especially mechanical treatment, for the latter, in spite of precautions, opens the way to impurities and to differences in treatment among the samples which are to be compared.

We have in most cases, therefore, made use of the diffusion method, the practical applications of which have been described by Moureu, Dufraisse, and Lotte[7] and which consists in impregnating the rubber with a solution of the substance to be tested. The sample of rubber to be treated is immersed for a given time in a titrated solution of the catalyst studied and after being taken out is dried *in vacuo*. The decrease in the weight or volume of the original liquid indicates the quantity of catalyst retained by the sample.

We have shown earlier[7] that substances thus deposited on the rubber penetrate progressively by diffusion to the interior of the mass, particularly if care has been taken to use a solvent, such as ether, which causes swelling.

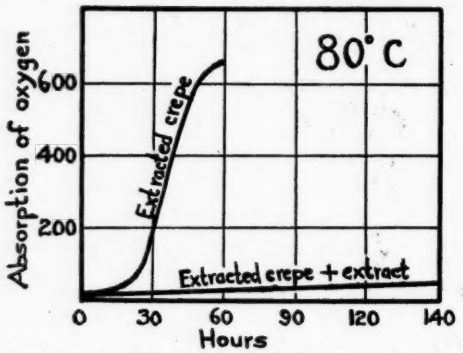


Figure 3—Effectiveness of Incorporation by Diffusion. Reincorporation of the Acetone Extract

The effectiveness of this method of incorporating catalysts has been verified more than once.[8] If further proof were required, it would be found in the experiments which are the subject of this work. We shall mention simply, in advance, two examples. A raw rubber, to which the antioxygenic resin, removed by acetone extraction, is again restored by diffusion, recovers its original resistance to oxidation (Fig. 3). Conversely, a positive catalyst (Figs. 25 and 27), copper acetylacetonate, used in the same way, caused a marked acceleration of oxidation.

The objection may be raised that diffusion gives a homogeneous mass only at the end of an indefinite period. We do not consider that this leads to any errors because in our method of investigation the tests are essentially of a comparative nature. Since the different samples are treated under comparable conditions and comparisons alone are desired, our experiments retain their value in the same way as if we had used homogeneous masses.

Moreover, a state of homogeneity is not reached with any certainty unless there is solution, and in the strict sense of the word, this is not realized even by mixing.

In any case, since the penetration of oxygen can take place only by diffusion, it is logical to employ the same means in introducing the catalysts which are

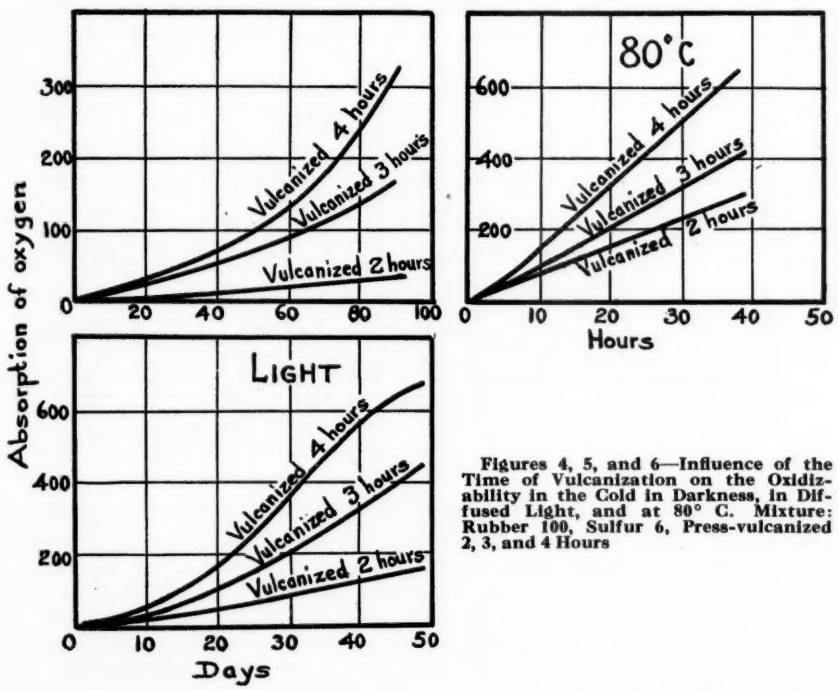
destined to intervene in the oxidation. Moreover, in this method the contexture of the samples is not modified, and errors arising from differences in the physical state are avoided.

Finally, the diffusion method is the only one applicable to experiments made after vulcanization, and these are naturally the most interesting because, after a rubber product is in its finished form, this is the only method that can be applied in a practical way.

After all, the two processes, mixing and diffusion, supplement one another.

C. Results

Because of its rapidity and its precision, our method leads to results which we believe are really new, and it is of interest that it confirms certain earlier observations of other authors.



Figures 4, 5, and 6—Influence of the Time of Vulcanization on the Oxidizability in the Cold in Darkness, in Diffused Light, and at 80° C. Mixture: Rubber 100, Sulfur 6, Press-vulcanized 2, 3, and 4 Hours

It is well known, for example, that the degree of vulcanization has an appreciable effect on the rapidity of the rate of deterioration.[5] The higher the degree of cure, the more susceptible is a rubber to deterioration, as is very evident in the curves of Figs. 4, 5, and 6, which give the rates of oxidation of rubber vulcanized with sulfur alone (the simplest case). In the cold, when hot, and in light, the rate of absorption of oxygen varies in proportion to the time of vulcanization. Moreover as Davey[9] has shown by another method, the effect of the time of vulcanization is more evident in the cold than when hot.

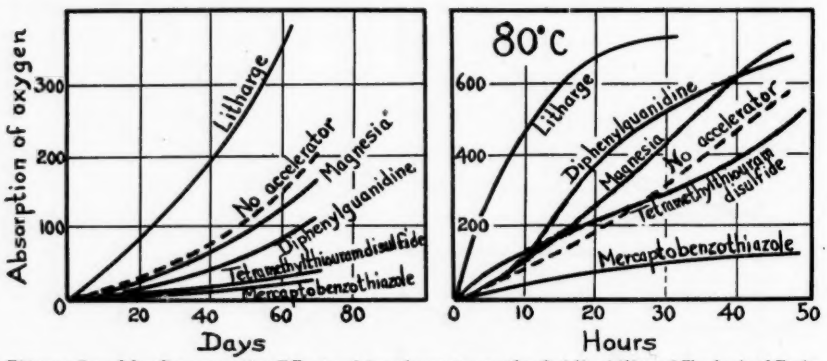
It seemed of interest to us in the course of these experiments to consider briefly the effect of other methods of vulcanization (Figs. 7 and 8). Two influences will be seen very distinctly, one a proöxygenic effect shown by litharge and another

an antioxygenic effect shown by mercaptobenzothiazole. We intend to return later to these phenomena in order to verify them and to carry them further.

II. Systematic Study of Various Influences Which Are Capable of Modifying the Tendency of Rubber to Oxidize

We shall review our earlier experiments on the causes which may modify the tendency of rubber to oxidize, and in this brief survey we shall concern ourselves particularly with the readiness with which our method distinguishes the different factors involved in the autoöxidation so that the various separate influences and the autoöxidation in the total effect will be recognized.

A first-latex pale crepe was used in the experiment. In general, vulcanization was carried out with sulfur alone (6 per cent, 4 hours at 143° under pressure) so as to use the simplest mixture possible. Nevertheless, other methods were also used, and these will be mentioned in the text. The vulcanized sheets were 1 millimeter thick. A study of rubber of different origin or treated differently has been left until a later time.



Figures 7 and 8—Comparative Effects of Accelerators on the Oxidizability of Technical Rubber Mixtures[10]

1. Acetone Extract

All the samples of rubber which were used contained, as we have already mentioned, substances which were known to have a marked effect on the tendency of rubber to oxidize,[11,12] *viz.*, the natural antioxygens. It seemed logical to us to ascertain first of all the mode of action of these substances and their influence.

a. Preparation of Acetone Extracts.—The crepe was cut in strips and extracted with acetone in the Soxhlet for 12 hours. We made certain that this time was sufficient to extract all the natural antioxygens (Fig. 11). The acetone extract was concentrated to a small volume and let stand for the deposit of crystals,[12] which were removed by drying. The clear liquid, evaporated to dryness, left a resin which was the acetone extract. The crepe studied gave about 0.5 per cent of crystallized product and 1.8 per cent of resins. According to Bruson, Sebrell, and Vogt[12] the antioxygenic property is localized in the resinous part of the extract. We verified this and found in our turn that the crystallized product has no appreciable antioxygenic action. In our tests, too, we discarded this crystallized portion and used only the resins.

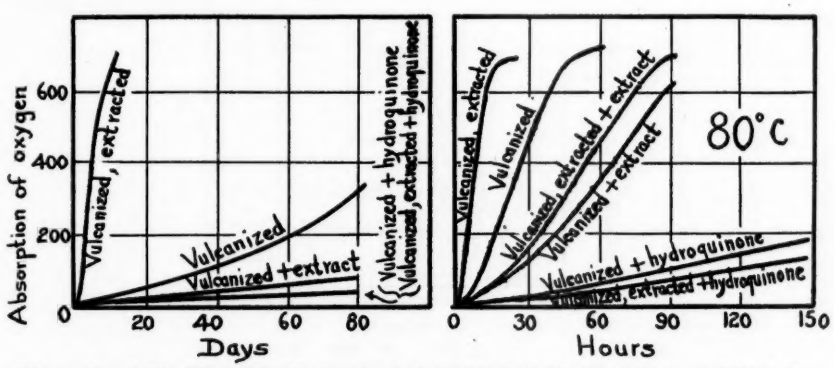
b. The Influence of the Acetone Extract on the Autoöxidation of Raw Rubber.—Raw pale crepe is extraordinarily stable toward oxidation, and it is indeed unfortunate that rubber after vulcanization is not equally resistant to atmospheric

oxygen, because the problem of protection against aging would be easily solved, or rather would not even be of any concern. In our experiments we have investigated the relations between the raw rubber and the acetone-soluble ingredients which it contains.

In the cold, our samples of raw rubber did not oxidize appreciably in 5 months in darkness. The experiment was continued, until we began to see the first signs of oxidation. Since the sensitivity of our method reached at least 0.0001 part by weight, or about 0.0002 molecule of oxygen per molecule of isoprene,[13] it is evident that oxidation of raw crepe in the cold and in darkness is less than 0.0001 part by weight in 5 months.[14] If this is compared with that of rubber vulcanized with sulfur (Fig. 4), for example, there is a fiftyfold difference, and a still greater difference must be expected when the experiment has reached completion.

Another sample was heated to 80° for 150 hours, or about 6 days. This experiment was interrupted because it threatened to last too long, in this case also, without visible oxidation.

It was necessary to work in the neighborhood of 130° in order to bring about an oxidation (and then only at the end of 9 hours). However, once started, the oxidation progressed very quickly.



Figures 9 and 10—The Slight Antioxygenic Activity of the Acetone Extract of Raw Crepe toward the Vulcanized Crepe. To the Latter 1.7% Was Added, *i. e.*, the Percentage in the Raw Crepe. The Same Percentage of Hydroquinone Was Added for Comparison

We then undertook to confirm the fact that the susceptibility to oxidation which rubber acquires, as is known by acetone extraction, is due above all not to a change in the substance but to the removal of its antioxygens. This was the object of the experiment shown in Fig. 3. If rubber is reimpregnated with its own extract which has been previously extracted by acetone, a product is obtained which has regained if not entirely, at least in large part, its original resistance to oxidation.

This experiment confirms and completes the results of earlier workers on the same subject, for our test was made without affecting the contexture of the samples.

According to what has been mentioned by several authors,[5, 9, 15, 16, 17] we observed in our turn a period known as "induction," *i. e.*, a period preceding the active phase of autoöxidation, during which the phenomenon proceeds only at an inappreciable rate. This phenomenon can be seen on some of the curves. This induction period is not peculiar to rubber; it has been observed in the case of other autoöxidizable substances.[18]

c. The Influence of the Acetone Extract on the Autoöxidation of Vulcanized Rubber.—What becomes during vulcanization of the antioxygenic impurities of the

acetone extract and of their protective action? Does not the destruction of these impurities impart to vulcanized rubber its susceptibility to deterioration? If this is so, it would be easy to restore to it the immunity it had in the raw state by renewing its normal content of acetone extract. An attempt has been made to answer this question by extracting the vulcanizate with acetone and by comparing the oxidations, on the one hand before and after extraction with acetone and on the other hand after the addition of a like proportion of fresh extract to the samples. The results in the cold and at 80° are shown on Figs. 9 and 10, as well as the effects of the addition of hydroquinone tested for comparison.

The antioxygenic properties were not entirely destroyed by vulcanization, since the vulcanized rubber when extracted with acetone became more sensitive to oxygen. The solvent therefore removed antioxygens from it.[19] However, it might be supposed that without being completely destroyed, the protective resins have lost to a great extent their original efficacy through modification or partial decomposition. This did not seem to be the cause of the tendency of rubber to oxidize after vulcanization, because the addition of a new portion of fresh acetone extract, even if it exercised an undeniable protective action on the vulcanizates

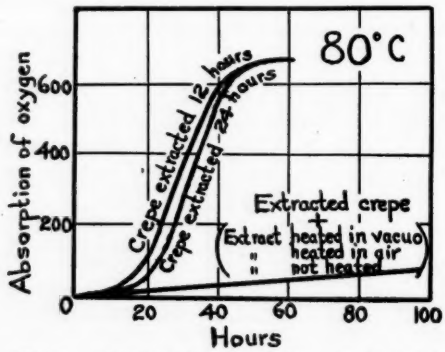


Figure 11—Stability of the Antioxygenic Properties of the Acetone Extract toward Heat and Oxygen

(extracted and not extracted), did not begin to give them the immunity that it does to raw rubber or even that which is imparted by an artificial antioxygen like hydroquinone. Thus the acetone extract, an ideal antioxygen for raw rubber, is, on the contrary, only a mediocre protective agent for the same rubber after vulcanization. Consequently, there is little to be hoped from a knowledge of its components in the acetone as a means of improving the resistance of the vulcanizate to oxidation.[20]

Incidentally, it may be concluded from these observations that the autoöxidation of vulcanized rubber is not of the same type as that of raw rubber, since it has not the same order of sensitivity toward the same catalysts. The problem of the stabilization is then strictly dependent upon the state of the rubber, and this should not be overlooked in practice.

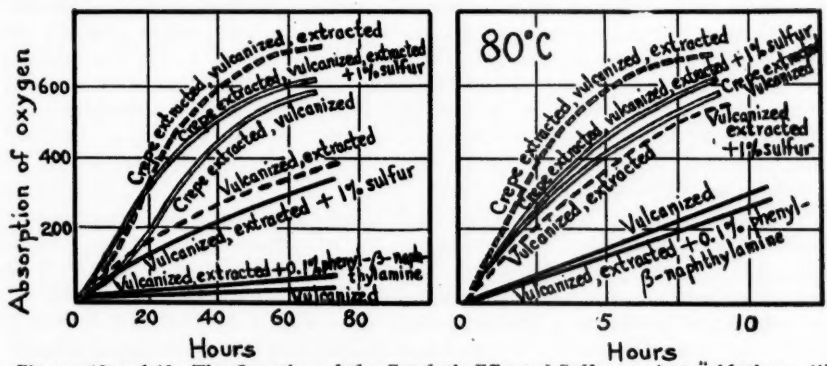
d. The Influence of the Acetone Extract on the Autoöxidation of Substances Other Than Rubber.—In order to obtain further information on the antioxygenic action of the acetone extract, it has been added to some autoöxidizable substances other than rubber and its effect has been compared with the effects of other substances of which the antioxygenic power had been shown in earlier studies. This com-

parison was made with hydrocarbons related to rubber (limonene and pinene) as well as with benzaldehyde. We shall return to this subject later, and shall mention here only that the activity of the extract classes it among good antioxygens.

e. Various Influences of the Acetone Extract on the Antioxygenic Power.—In view of the activity of this substance and also from the fact that it is present in different rubber products, some experiments were made to determine its resistance to heat. A sample, divided into two parts, was heated at 127° for 9 hours, both *in vacuo* and in the air. Fig. 11 shows that, if not the resin itself, at least its antioxygenic power is very resistant to heat, even in the presence of air.

On the other hand, the curves in Fig. 10 make it appear as if the antioxygenic power was changed somewhat by vulcanization. In fact, there was less protection when the extract which had undergone the vulcanization process was left in the rubber (curve marked "vulcanized") than when it was replaced by an equivalent quantity of fresh extract, the former having naturally been eliminated by acetone extraction (curve marked "vulcanized, extracted + extract").

Accordingly, the extract is partially altered by vulcanization, but according to the preceding facts, this should not be attributed to heat alone, and moreover this alteration is not sufficient to explain the tendency of vulcanized rubber to oxidize.



Figures 12 and 13—The Question of the Catalytic Effect of Sulfur on Autoöxidation. (1) Vulcanized Rubber Extracted with Acetone (Solid Curves). (2) Crepe Extracted with Acetone, Vulcanized with Sulfur, Then Extracted with Acetone (Dotted Curves)

In view of the influence of the extract, which at times is considerable, in most of the experiments which follow, it has been eliminated so as to avoid complications and uncertainties which might result from its presence. Nevertheless, in every experiment care has been taken to run a "blank," that is to say, a sample subjected to the same tests as the other but still containing its extract.

2. Sulfur

Sulfur is doubtless one of the substances, the action of which it is most desirable to understand. On the one hand, it is necessarily present in the free state in all manufactured products, and on the other hand our general preliminary studies revealed its very striking effects on autoöxidation. For example, benzaldehyde[21] is not oxidized when it has a sulfur content of only 0.001 per cent, and the oxidation is greatly retarded by very much smaller proportions. In the same way, with respect to hydrocarbons, more or less intense antioxygenic influences have at times been found, as in the autoöxidation of paraffins[22] with heat. On the contrary, sulfur has almost no effect on the autoöxidation in the cold of styrolene, of pinene,[23] and of limonene.

The experiments were carried out only with vulcanized rubber because the oxidation of raw rubber, even when deprived of its resins, is too slow in the cold. For the present, therefore, we cannot deal with these experiments. As for tests at elevated temperatures, it is not necessary to consider these any further, for when heating at 80° is prolonged at all a progressive vulcanization sets in, a change which it has just been shown has a considerable influence on the tendency to oxidize. In this case there would be two superimposed reactions without any means of distinguishing the part played by each one.

Vulcanized rubber was extracted with acetone, in such a way as to remove not only all its resins but also the free sulfur. One sample was retained as a control and 1 per cent sulfur was added to the other part. The two were then subjected to the action of oxygen, both in the cold and at 80°. Figs. 12 and 13 (curves in solid lines) show that the oxidations of the two samples have almost identical courses, and consequently sulfur seems to be without effect on the rate of the autoöxidation of vulcanized rubber. For comparison one sample was treated with an industrial antioxygen, *viz.*, 0.001 per cent of phenyl-β-naphthylamine.

For the purpose of finding out if the resins exert a disturbing influence because of their reaction with sulfur during vulcanization, the following tests were made. The resins were removed from a raw rubber by acetone extraction, and after vulcanization the rubber was again extracted with acetone, which removed the free sulfur. This was divided into two samples, to one of which was added 1 per cent of sulfur. Graphs 12 and 13 (curves with broken lines) show that the effect of the sulfur is very slight and is practically negligible. Consequently, the free sulfur does not seem to influence the oxidation either one way or the other, *i. e.*, in the same way as with other ethylenic hydrocarbons, it is neither an accelerator nor a retarder.

This contrast, where a given substance is at one time inert and at another time has a high catalytic activity according to the conditions is one of the greatest curiosities of antioxygenic catalysis. We may recall in this connection that the change in the behavior of a catalyst may even extend to an inversion of the catalyst, an antioxygen becoming a proöxygen and *vice versa*, a phenomenon known as inverse catalysis,[24] in which there is close relationship between the two effects, and of which further examples will be found later in connection with the stabilization of rubber. The importance of these ideas for industrial practice cannot be exaggerated. In any case the sensitivity which rubber acquires after vulcanization cannot be attributed to the presence of excess sulfur any more than sulfur can be considered to play any notable protective role. Consequently, in experiments on catalysis, one need not, in general, count upon any disturbing effect by the sulfur, except, of course, its direct chemical effect on the catalyst.

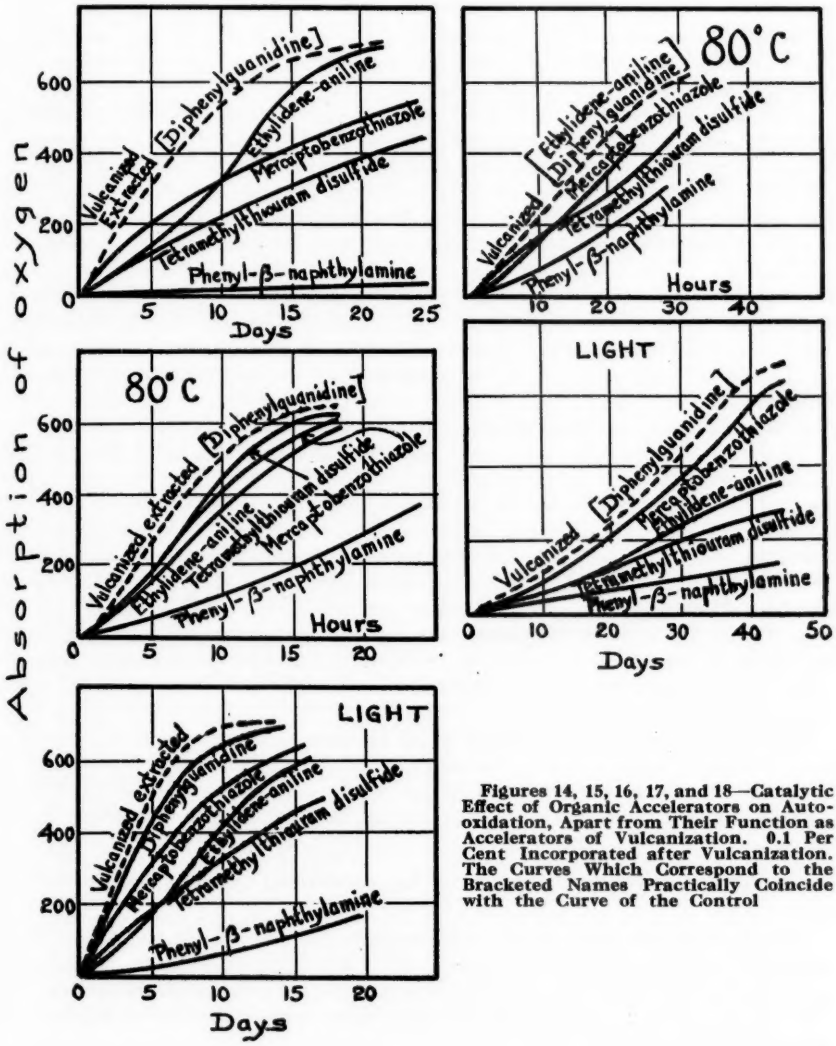
3. Accelerators

According to the preliminary experiments referred to above, the resistance of vulcanized rubber to oxidation is increased by the use of certain accelerators such as mercaptobenzothiazole. This observation agrees with the well-known fact that the use of organic accelerators usually prolongs the life of manufactured products.

Moreover, from our general earlier investigations, it might be supposed that the molecules of organic accelerators would because of their chemical nature be catalysts of autoöxidation. This we have in fact proved.

There is therefore a twofold reason for studying the influence of accelerators on the autoöxidation of rubber, considered apart from their action on vulcanization.

In order to limit the experiments under consideration, which are already very numerous, the investigation was carried out only with some common accelerators, including ethylidene-aniline, mercaptobenzothiazole, tetramethylthiouram disulfide, and diphenylguanidine.



Figures 14, 15, 16, 17, and 18—Catalytic Effect of Organic Accelerators on Autoxidation, Apart from Their Function as Accelerators of Vulcanization. 0.1 Per Cent Incorporated after Vulcanization. The Curves Which Correspond to the Bracketed Names Practically Coincide with the Curve of the Control

Rubber vulcanized without accelerators was divided into two parts, one of which was extracted with acetone, and then the two were treated with 0.1 per cent of the accelerators.

This proportion might seem very small, but in view of the very intense action of certain antioxygens those which do not show appreciable effects with 0.1 per cent

must be considered relatively weak. It is therefore not necessary for preliminary classification to resort to large proportions.

At ordinary temperature[25] as well as at 80°, and in diffused light, the results shown (Figs. 14, 15, 16, 17, and 18) were obtained. Diphenylguanidine is almost without effect, ethylidene-aniline, mercaptobenzothiazole, and tetramethylthiouram disulfide have, most of the time, a distinct but weak antioxygenic influence. Consequently, aside from diphenylguanidine, the accelerators have an antioxigenic action which is not negligible, but is lower than that found for other substances (see the curves of phenyl-β-naphthylamine).

Certain differences were found in the effect on the tendency to oxidize, according to whether the addition of the accelerators was before vulcanization (like accelerators in Figs. 7 and 8) or after vulcanization (like antioxygens in Figs. 14, 15, 16, 17, and 18). Doubtless the differences observed are to be attributed in part to the differences in the concentration of the accelerators, and we refrain from drawing conclusions from this comparison, which we plan to consider in a separate investigation.

Thus the accelerators have only a slight influence on the autoöxidation of rubber, contrary to what might be thought from their compositions. The question then arises whether they are not more active toward other substances. This property is not without some use, for at times rubber may contain oxidizable substances which require protection, in their turn. Should not accelerators be capable under some conditions of playing the part of protective agents?

Limonene, pinene, styrolene, and benzaldehyde were treated with the four accelerators. Mercaptobenzothiazole has no effect on limonene, whereas tetramethylthiouram disulfide and diphenylguanidine retard slightly the time when oxidation starts. Ethylidene-aniline is a good antioxygen. Diphenylguanidine has little effect on pinene, whereas the other three have an intense negative effect. With styrolene, diphenylguanidine has a remarkable proöxygenic effect. This catalyst is characterized by an alarming tendency which must be taken into account in its use as an accelerator and in the use of mixtures containing it. The oxidation of benzaldehyde is slightly retarded by mercaptobenzothiazole, whereas ethylidene-aniline and tetramethylthiouram disulfide are very powerful antioxygens.

In short, the accelerators studied, which are poor antioxygens for rubber, often have a high catalytic power in the oxidation of other substances. Moreover, one of them showed a marked proöxygenic effect. On the whole, the effect of a catalyst was found to vary with the autoöxidizable substance with which it was used.

4. Catalysts, Properly Speaking, of Autoöxidation: Antioxygens and Prooxygens

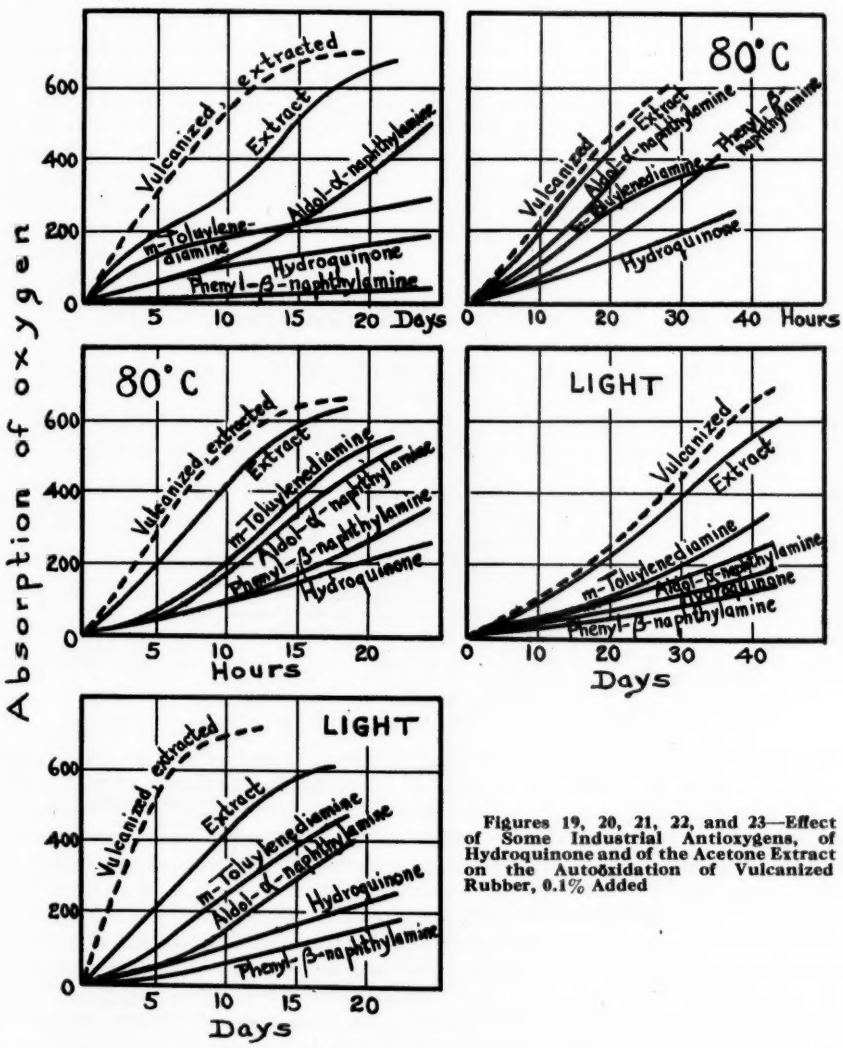
Having reviewed the different substances which are almost indispensable in rubber,[26] we now come to substances which are, strictly speaking, catalysts of autoöxidation, that is to say, to substances the principal effect of which is to modify the rate of oxidation, either in the favorable sense (antioxygens) or in the harmful sense (proöxygens).

We investigated first the action of some commercial products which are still incorrectly called antioxidants,[27] so as to study the relations between their well-known anti-aging power[28,29] and their antioxygenic properties, determined by our procedure.

Three products were then compared: phenyl-β-naphthylamine, aldol-α-naphthylamine, and *m*-toluylenediamine, and the most polyvalent antioxygen which

our general preliminary investigations had disclosed, hydroquinone, was included. The experiments were carried out on vulcanized rubber, extracted with acetone and not extracted in the cold, at 80°, and finally in diffused light.

At a concentration of 0.1 per cent they were classified as follows (Figs. 19, 20, 21, 22, and 23). On the one hand, hydroquinone and phenyl-β-naphthylamine



Figures 19, 20, 21, 22, and 23—Effect of Some Industrial Antioxygens, of Hydroquinone and of the Acetone Extract on the Autoöxidation of Vulcanized Rubber, 0.1% Added

had a similar intensity of action, the other two, aldol-α-naphthylamine and *m*-toluylenediamine make up a second group that is still good, but less effective than the preceding.

"Threshold" solutions were then studied, *i. e.*, solutions of a lower limit of concentration at which a distinct effect begins to appear. These tests showed at

ordinary temperature and in darkness a limit in the order of magnitude of 0.002 per cent for phenyl-β-naphthylamine and of about one-half that for hydroquinone (Fig. 24).

The effects of the industrial antioxygens on the autoöxidation of substances other than rubber (pinene, limonene, and benzaldehyde) were tested in the same way as was the case with the accelerators. As a comparison, the natural resin of raw crepe and hydroquinone were tested at the same time. With 0.1 per cent, all these substances have a powerful retarding effect. It is thus rather curious to find a similarity of behavior in the natural and artificial protective agents of rubber. An examination of the curves suggests certain other points. As usual, the effect of each catalyst varies with the autoöxidizable substance with which it is used; the best antioxygen in one case may be less effective in another case. Attention should also be called to the intensity of the antioxygenic effects exerted on substances which are easily oxidized, in contrast to the small effect on rubber. This contrast is shown plainly by the simple appearance of the graphs.

In this way, in spite of the progress toward the stabilization of rubber, there is still a great deal to be done, judged by other oxidizable substances. We hope

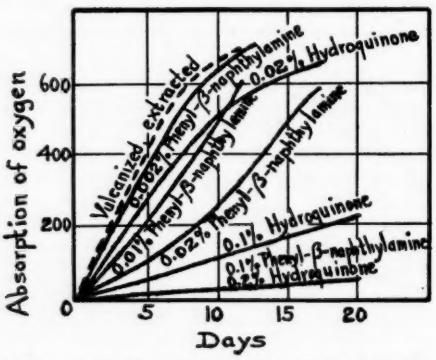


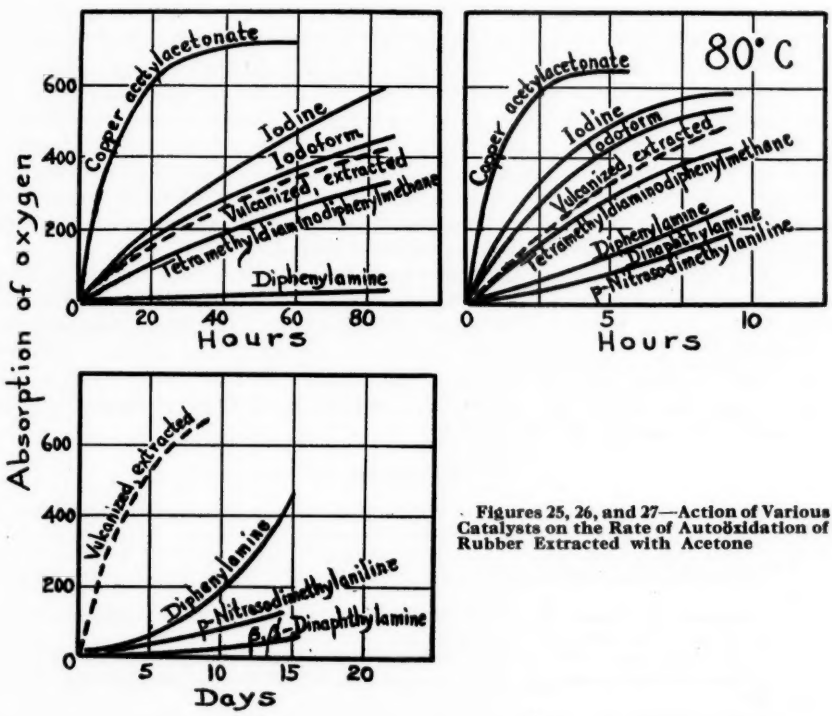
Figure 24—The Threshold of Antioxygenic Activity of Hydroquinone and of Phenyl-β-Naphthylamine toward Vulcanized Rubber

therefore to undertake a systematic study of the subject, commencing with a long series of catalysts. Figs. 25, 26, and 27 represent the beginning of this work, and show the effect on the autoöxidation of rubber of several catalysts selected at random among those already studied in the laboratory. The marked antioxygenic effects of β,β-dinaphthylamine, *p*-nitrosodimethylaniline, and diphenylamine, and above all a remarkable example of the inversion of a catalytic action, copper acetylacetonate, which exerts a strong antioxygenic effect on limonene but on the contrary a strong proöxygenic effect on rubber (Figs. 25 and 27), should be noted as salient facts. We have already pointed out many times the variations in the effects of the same catalyst, which are evident both from our earlier work and from the curves in the present paper. The case of the copper salt illustrates further this phenomenon, and it shows what large errors may be made if the catalytic effect observed with one substance is assumed, without checking, to be true of another substance, solely because they are similar chemically or related in some way, as in the case of pinene, limonene, and rubber.

This variation in the catalytic effect depends not only upon the nature of the oxidizable substance, but also upon the different conditions which are involved in

the autoöxidation. It was therefore to be expected that the physical agents, heat and light, would have a further disturbing effect upon the phenomenon, and their influence was taken into account.

In reality, the order of activity of antioxygens is not the same in the cold and when hot; thus from Figs. 19 and 20, phenyl-β-naphthylamine appears to be more active in the cold (darkness) than at 80°, whereas hydroquinone has a more nearly constant action. The same type of variations were seen above for rubber vulcanized with organic accelerators (Figs. 7 and 8). With mercaptobenzothiazole the stability seemed to remain constant in the cold and at 80°, whereas with the other three it diminished at the elevated temperature.



Figures 25, 26, and 27—Action of Various Catalysts on the Rate of Autoöxidation of Rubber Extracted with Acetone

In accordance with certain observations of earlier authors, our determinations show a similarity in the influence of heat and of diffused light, with, however, certain distinctive characteristics evident on Figs. 20 and 21 on the one hand, and 22 and 23 on the other. We are able to show only a summary of these results.

Without doubt it has been noticed how small the proportions of antioxygens were; this is because our technic is sufficiently sensitive to detect with precision effects which are very slight. This is of appreciable advantage because with high proportions the length of time required for changes to take place is excessively prolonged, and this limits the number of tests. Otherwise one must resort to a "forced" oxidation (heating, pressure), of which the more artificial character introduces an element of uncertainty which it is best to avoid.

Conclusions

This first series of experiments was aimed to establish the value of the method of study which is described, and to indicate its applications. Furthermore, we were less interested in going deeply into the various problems considered than to show by the various examples the convenience and the precision of our method. There still remains the problem of determining the relation between autoöxidation observed in this way and true aging by ordinary methods. This will be a task for the future. However, as far as we have gone in this work, a satisfactory parallelism has often been found between our data and that already obtained by the usual methods.

Although we have not made a detailed study of some of the results, we have been led to a certain number of concrete conclusions in the course of the study. Two of them are worthy of being mentioned. One concerns the variation of the action of every catalyst of autoöxidation, the other the future of methods of protection.

Moureu and Dufraisse have already emphasized the sensitivity of autoöxidation catalysts to the slightest influences, and this is again confirmed in the case of rubber. Consequently, a catalyst, whatever may be its properties, should not be classified as a good antioxygen in general. It should receive this qualification only for precise conditions where its efficacy has been effectively controlled, because its influence is subject to variations which may extend as far as a change in the sign, oxidation then being accelerated instead of retarded.

In regard to the future of the protection of rubber, it is easy to predict from what has been found for other oxidizable substances. Remarkable progress has already been made in the industrial use of antioxygens. Instead of continuing to evaluate them by certain units, the coefficient of protection should be calculated by powers of 10, as with so many other substances. In that case, rubber, at last really stabilized, would find vast markets opened up in which it cannot be used at present on account of its instability.

References

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[2] See also Porritt, *Trans. Faraday Soc.*, **16**, Appendix, p. 81 (1920).

[3] Moureu, Dufraisse, and Badoche, *Compt. rend.*, **179**, 1229 (1924); *Bull. soc. chim.*, **35**, 1564 (1924).

[4] Staudinger and Leupold, *Ber.*, **63**, 730 (1930); "Conseil de Chimie Solvay" (1931).

[5] Kohman, *J. Phys. Chem.*, **33**, 235 (1929).

[6] See Marzetti, *Giorn. chim. ind. applicata*, **5**, 122 (1923); Bruni, *India Rubber J.*, **63**, 814 (1922).

[7] Moureu, Dufraisse, and Lotte, *Ind. Eng. Chem.*, **22**, 549 (1930); *Rev. gén. caoutchouc*, No. 63, July, **1930**.

[8] See in particular, Semon, Sloan, and Craig, *Ind. Eng. Chem.*, **22**, 1001 (1930).

[9] Davey, *Trans. Inst. Rubber Industry*, **6**, 202 (1930).

[10] Vulcanization under pressure at 143°; Crepe 100, sulfur 6 (4 hrs.); crepe 100, sulfur 6, litharge 5 (1 hr.); crepe 100, sulfur 2.5, zinc oxide 5, mercaptobenzothiazole 0.8 (30 min.); crepe 100, sulfur 6, magnesia 1 (1 hr.); crepe 100, sulfur 3.5, diphenylguanidine 1, zinc oxide 5 (45 min.); crepe 100, sulfur 2.5, zinc oxide 5, tetramethylthiouram disulfide 0.4 (10 min.).

[11] Whitby, Dolid, and Vorston, *J. Chem. Soc.* (London), **1926**, 1448.

[12] Bruson, Sebrell, and Vogt, *Ind. Eng. Chem.*, **19**, 1187 (1927).

[13] If necessary, this sensitivity could be still further increased without difficulty.

[14] Since the solubility of oxygen in rubber is weak (Williams and Neal, *Ind. Eng. Chem.*, **22**, 874 (1930)) any uncertainty about the degree of saturation of the mass is of no concern.

[15] Peachey, *Chemistry and Industry*, **31**, 1103 (1912).

[16] Peachey and Leon, *Ibid.*, **37**, 55T(1918).

[17] Leon and Lister, *Ibid.*, **46**, 220T (1920).

[18] See particularly, Moureu, Dufraisse, and Chaux, *Chimie et industrie*, **18**, 3 (1927).

[19] It will be seen later that free sulfur is not concerned here.

[20] In passing it should be mentioned that these experiments can only be carried out after vulcanization, and consequently require the use of the diffusion method. Other similar experiments will be found later.

[21] Moureu and Dufraisse, *Compt. rend.*, **178,** 1861 (1924).

[22] Moureu, Dufraisse, and Chaux, *Chimie et industrie*, **18,** 3 (1927).

[23] Moureu, Dufraisse, and Badoche, *Compt. rend.*, **179,** 237 (1924).

[24] Moureu and Dufraisse, *Chem. Reviews*, **3,** 113 (1926); *Chemistry and Industry* (Messel Memorial Contribution), **47,** 819 (1928); see also Dufraisse, *Revue scientifique*, July, **1930**.

[25] Tests were made only with rubber extracted with acetone.

[26] In this first study we disregard provisionally dyes, fillers, factice, reclaimed rubber, etc.

[27] Before his death, Charles Moureu strongly urged the suppression of the term "antioxidant" (*Ind. Eng. Chem.* **22,** 549 (1930); *Rev. gén. caoutchouc*, No. 63, July, 1930). In respect of his memory we again ask that the term be given up. Moreover since this term is incorrect there is danger of error: an antioxygen is not an antioxidant.

[28] Weber, *Ind. Eng. Chem.*, **18,** 963 (1926).

[29] The subject of the application of antioxygens to the rubber industry has been discussed in an excellent fashion by L. Sloïm, *Encyclopédie du Caoutchouc*, Syndicat du caoutchouc éditeur, Paris, and also by Naunton, *Trans. Inst Rubber industry*, **5,** 317 (1930).

[Translated from Revue Générale du Caoutchouc, Vol. 8, No. 77, pages 5–6, December, 1931.

Applications to Rubber of the Concept of Antioxygens and Proöxygens

The Case of Litharge

Charles Dufraisse and Nicolas Drisch

It is known that the oxidation of autoöxidizable substances can be retarded or accelerated by the addition of a small proportion of certain compounds. To these latter Moureu and Dufraisse have given the name antioxygens and prooxygens, have shown that they act catalytically, and have proposed a theory to explain their action.[1]

Like other autoöxidizable substances, rubber is sensitive to pro- or antioxygenic catalysis, and this fact is of particular interest, since autoöxidation is one of the principal causes of its spontaneous deterioration or aging.

It seemed worth while therefore to undertake a systematic study of this oxidation, with the hope of drawing practical conclusions in connection with industrial processes and the preservation of rubber. The change brought about by autoöxidation is a complex phenomenon, and only when each of the factors is studied separately can exact conclusions be reached. In our case we have tried to distinguish each of the influences which may play a part.

In our study we used the experimental method of Moureu and Dufraisse, which in principle involves measuring the rate of oxidation by the manometric method in the cold and at 80°. Since earlier observations and our own preliminary experiments showed that oxygen in the proportion of 1 to 100 was sufficient to make the rubber useless, all our experiments are concerned only with the beginning of oxidation.

In the first paper presented at the Congress of Rubber Technologists,[2] the various factors which influence the oxidizability of rubber were studied. Particular attention was paid to the time of vulcanization, to sulfur, to the acetone extract of raw crepe, to accelerators, and to a few common antioxygens. The results obtained in the study of oxidation were in many cases in complete accord with observations made earlier in an investigation of aging. However, a comparative examination of the oxidizability of rubber vulcanized in the presence of different accelerators showed that the mixture vulcanized in the presence of litharge had a great tendency to oxidize. The rate of oxidation of this rubber was much greater than that of the simple rubber-sulfur mixture.

This fact, which has appeared to us to be abnormal, has somewhat surprised technologists.[3] In reality, litharge incorporated in a mixture makes curing in hot air possible, which gives it the reputation of protecting rubber against oxidation during vulcanization, in other words, the reputation of being an antioxygen. This is contrary to what we have observed, for according to our experiments litharge should act as a proöxygen. Faced with such a contradiction, it was necessary to undertake a detailed study of this phenomenon.

Our new experiments were carried out first on mixtures prepared with pure rubber, later with industrial mixtures.

Quite naturally we were concerned with confirming our earlier experiments. In order to avoid an error from overcuring the samples, we determined the oxidizability of two mixtures with 5 and 10 per cent of litharge, which had been vulcanized for increasing periods. In the cold and at 80°, regardless of the state of cure, the tendency to oxidize was found to be greater than that of a sample vulcanized in the presence of diphenylguanidine, which was chosen because of its great tendency to oxidize. It was therefore litharge which had had an accelerating effect in our early experiments.

Nevertheless, another objection may be raised to this. In our regular experiments, as was mentioned above, the quantity of oxygen absorbed by the rubber was one per cent at the most; should not, therefore, the abnormal absorption of oxygen be attributed to an oxidation of the lead sulfide formed during the cure, thus $PbS + 2O_2 \longrightarrow PbSO_4$?

This objection is perhaps less serious than would appear at first sight. In fact, when one autoöxidizable substance is mixed with another which is also capable of being oxidized, the oxidation of the first often accelerates that of the second. This classic phenomenon has even received a special name. It is called induced or "coupled" oxidation. For this reason the oxidation of lead sulfide must probably be harmful to the rubber itself.

Whatever the answer to this problem, in a special experiment where the rubber had absorbed a much greater quantity of oxygen than that necessary to saturate lead sulfide, no abnormality was found in the absorption curve; the oxidation of lead sulfide, if it does occur, represents only a small part of the oxygen absorbed.

Since all the experiments made on mixtures with pure rubber confirmed our earlier conclusion that litharge is a proöxygen with respect to rubber, we carried out experiments with some industrial mixtures. The experiments were made with samples prepared for physical tests. Here, too, the tendency of these mixtures to oxidize was much greater than that of rubber mixtures which did not contain litharge.

We then tried with oxidized samples to determine the variation in physical properties for a known quantity of absorbed oxygen by comparing this variation with that found in a control diphenylguanidine mixture. These experiments are still unfinished. The results obtained by oxidation at 80° may, however, be suggested by the fact that when two mixtures, accelerated in the first case by litharge and in the second by diphenylguanidine, had absorbed 0.7 per cent oxygen, the tensile strength of the first had diminished 40 per cent of its value and that of the second 80 per cent of its value.

In conclusion, it was proved that litharge, contrary to its reputation, is a prooxygen for rubber. It remains to explain the good effect which litharge has during hot-air vulcanization. This is the object of experiments now in progress.

References

[1] See the various publications of Moureu and Dufraisse on this subject, including a general discussion in the *Révue Scientifique*, **1930**.

[2] Congrès des Techniciens du Caoutchouc; *Rev. gén. caoutchouc*, **8**, No. 75, 39–55 (1931).

[3] See the discussion appended to the article in *Rev. gén. caoutchouc*, **8**, No. 75, 39–55 (1931).

[Translated from Revue Générale du Caoutchouc, Vol. 8, No. 75, pages 133–136, October, 1931.]

The Influence of Certain Accelerators on the Aging of Rubber

G. Martin and R. Thiollet

Among the accelerators which are at present on the market two are very much used, *viz.*, diphenylguanidine as an accelerator of medium activity, and tetramethylthiouram disulfide as a rapid accelerator.

Diphenylguanidine is used most of the time in proportions between 0.5 to 1 per cent, based on the rubber, and with about 3 per cent of sulfur.

Tetramethylthiouram disulfide is used in proportions of between 0.2 and 0.5 per cent, based on the rubber, with about 1.8 per cent of sulfur.

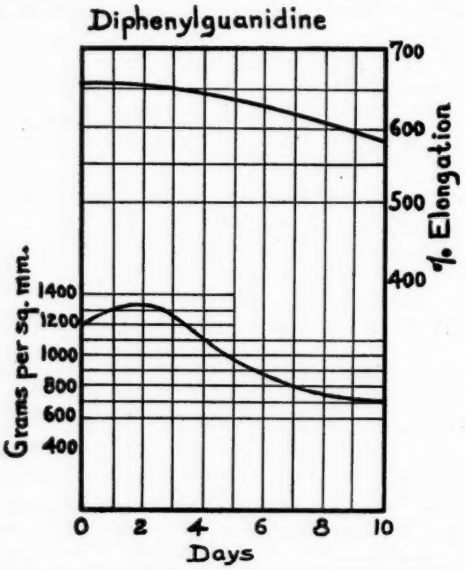

Figure 1—Aging of a Mixture Accelerated with Diphenylguanidine

In this way "nervy" mixtures are obtained which have excellent physical properties; but it must be recognized that these two accelerators are, each in its class, the ones which impart to mixtures the poorest aging qualities. For example, the mixture:

Pale crepe	100
Zinc oxide	5
Sulfur	3
Palm oil	1
Stearic acid	0.5
Diphenylguanidine	0.7

vulcanized 1 hour at 3 kilograms pressure, *i. e.*, under conditions which lead to the best physical properties for the proportions used, was investigated.

To study the aging of this mixture, ring samples cut from vulcanized sheets were

put in a ventilated oven heated by an electric resistance, where a regulator maintained a constant temperature of 70° C. Every other day 3 test pieces were taken from each mixture. Tests were made after 24 hours' rest; accordingly, each value represents the average of 3 tests. The test lasted 10 days.

By plotting the times of heating as abscissa and the tensile strengths as ordinate, curves were obtained which showed the way in which the tensile strength of vulcanized mixtures varied with increased heating. Similar curves were obtained for the per cent elongation at rupture.

In Fig. 1 the time of heating in days is shown on the X-axis.

The curve farthest from the X-axis represents the per cent elongations at rupture, indicated on the Y-axis at the right.

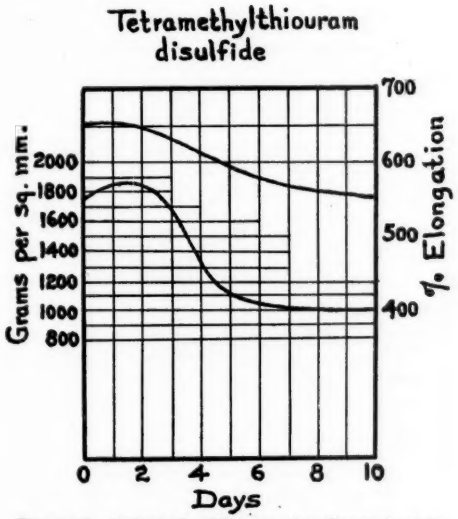

Figure 2—Aging of a Mixture Accelerated with Tetramethylthiouram Disulfide

The curve located nearest the X-axis represents the tensile strength in grams per square millimeters and is indicated on the Y-axis at the left.

In the same way the following mixture:

Pale crepe	100
Zinc oxide	5
Sulfur	1.8
Palm oil	1
Stearic acid	0.5
Tetramethylthiouram disulfide	0.4

vulcanized 10 minutes at 2 kilograms' pressure gave curves similar to those for the mixture vulcanized with diphenylguanidine. The results are shown in Fig. 2.

Figures 1 and 2 gave evidence of a rapid diminution in the physical properties of the two mixtures.

If A is the per cent elongation at rupture and C the load at rupture, the product $A \times C$ gives an indication of the quality of a mixture.

Accordingly, we can interpret the results of these tests by comparing the products $A \times C$ before heating in the oven and after heating. In this way it was proved

that both these products, after artificial aging for 10 days, lost more than 50 per cent of their quality.

It was then a question of determining the conditions of vulcanization under which the percentage loss of the product of $A \times C$ was the least after artificial aging.

Diphenylguanidine.—It has already often been observed that it is advantageous to reduce the time of vulcanization if mixtures with good properties are desired. Industrially, for practical reasons, the tendency is more and more toward a reduction in the time of vulcanization.

An investigation was made of the proportions of sulfur and diphenylguanidine used to vulcanize the following pure gum mixture for 25 minutes at 3 kilograms'

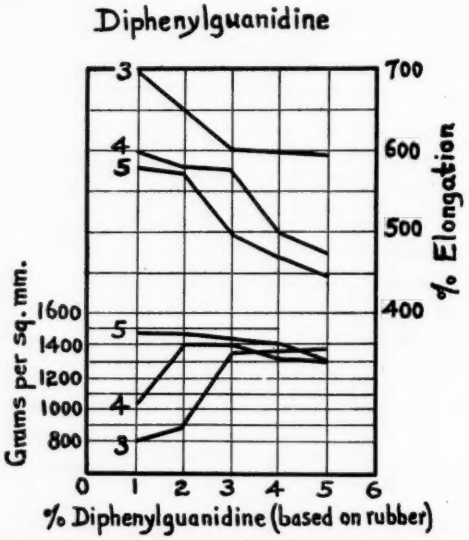

Figure 3—Physical Properties of Mixtures Containing Different Proportions of Diphenylguanidine

pressure; the time of 25 minutes was selected after several preliminary experiments.

Pale crepe	100
Zinc oxide	5
Stearic acid	0.5
Palm oil	1
Sulfur	...
Diphenylguanidine	...

For this purpose a series of mixtures (Fig. 3) was made containing:

(1) 1 per cent sulfur + 1, 2, 3, 4, and 5 per cent diphenylguanidine
(2) 2 per cent sulfur + 1, 2, 3, 4, and 5 per cent diphenylguanidine
(3) 3 per cent sulfur + 1, 2, 3, 4, and 5 per cent diphenylguanidine
(4) 4 per cent sulfur + 1, 2, 3, 4, and 5 per cent diphenylguanidine
(5) 5 per cent sulfur + 1, 2, 3, 4, and 5 per cent diphenylguanidine

These experiments proved that mixtures containing only 1 and 2 per cent sulfur do not vulcanize in 25 minutes at 3 kilograms, whatever the proportion of accelerator used.

With regard to the mixtures containing 3 per cent sulfur, curves were obtained showing the tensile strength and the per cent elongation at rupture with increase in the proportion of accelerator.

An examination of the curves proves that the tensile strength at rupture increases with increase in the proportion of diphenylguanidine up to 3 per cent and then remains constant. The elongation decreases with increase in the proportion of diphenylguanidine from 1 to 3 per cent, and then remains constant.

Similar curves were obtained for mixtures containing 4 and 5 per cent of sulfur.

The tensile strength of the mixture containing 4 per cent of sulfur remained constant for 2 and 3 per cent of diphenylguanidine, then decreased slightly with greater proportions of accelerator. The tensile strength of the mixture containing

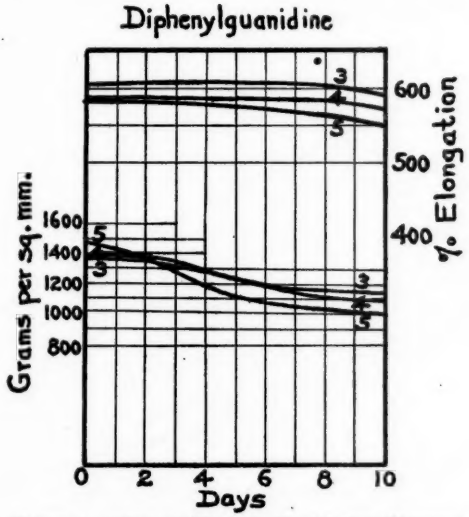

Figure 4—Aging of Mixtures Containing Different Proportions of Diphenylguanidine

5 per cent sulfur was constant for 1 and 2 per cent of diphenylguanidine, then decreased with higher proportions of accelerator.

The per cent elongation at rupture of the mixtures containing 4 and 5 per cent of sulfur decreased steadily with increase in the proportion of diphenylguanidine.

This shows that the best proportions of sulfur and of accelerator to vulcanize the pure gum mixture are the following:

	%	%	%
Sulfur	3	4	5
Diphenylguanidine	3	2	1

With regard to the aging tests of the vulcanized mixtures, curves were drawn by the same method as before (see Fig. 4).

An examination of these curves proves that the physical properties changed relatively little after artificial aging for 10 days.

For the mixture containing 5 per cent sulfur and 1 per cent diphenylguanidine, the product $\frac{AC}{10{,}000}$ dropped from 83.5 to 55, a decrease of about 34 per cent.

For the mixture containing 4 per cent sulfur and 2 per cent diphenylguanidine,

the product $\frac{AC}{10,000}$ dropped from 82.5 to 63.8, a decrease of about 22.5 per cent.

For the mixture containing 3 per cent sulfur and 3 per cent diphenylguanidine, the product $\frac{AC}{10,000}$ dropped from 81 to 69, a decrease of about 15 per cent.

For a vulcanization of 1 hour with 3 per cent sulfur and 0.7 per cent accelerator, the decrease was about 50 per cent.

It may therefore be concluded from these experiments that the best proportions of sulfur and accelerator to use in order that a pure gum mixture vulcanized 25 minutes at 3 kilograms may age well are:

	%
Sulfur	3
Diphenylguanidine	3

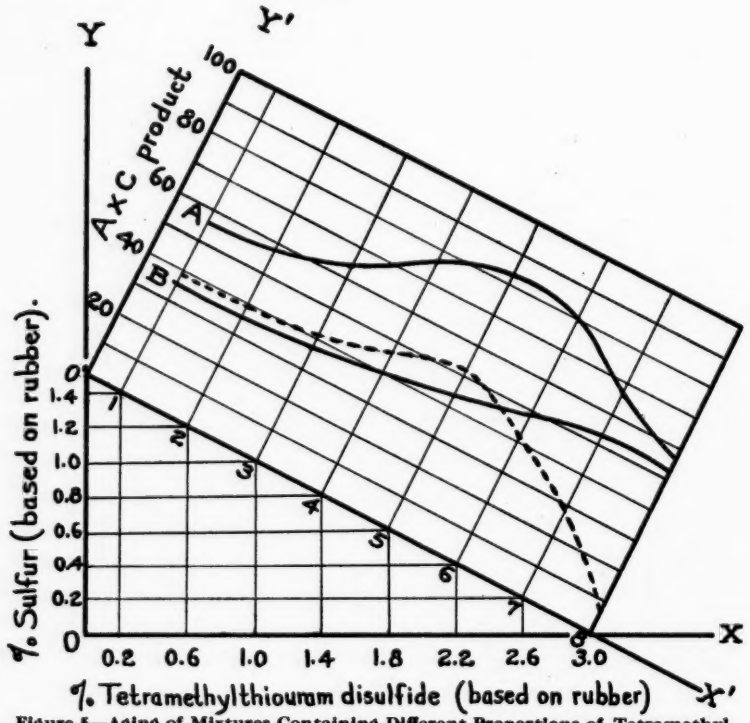

Figure 5—Aging of Mixtures Containing Different Proportions of Tetramethylthiouram Disulfide

Tetramethylthiouram Disulfide.—To obtain vulcanized articles aging as well as possible, the tendency is to reduce the proportion of sulfur. In this way it is possible to vulcanize with 1.4 per cent sulfur and 0.2 per cent tetramethylthiouram disulfide.

With rectangular coördinates, let the abscissa represent the proportions of tetramethylthiouram disulfide and the ordinate the proportion of sulfur (Fig. 5).

Join by a straight line the following points on the coördinates: $X = 0.2$, $Y = 1.4$, to the points of the coördinates: $X = 3$, $Y = 0$.

There is thus obtained a straight line whose equation is

$$Y = 1.5 - \frac{X}{2}$$

When "Y" equals successively 1.4, 1.2, 1, ... 0.4, 0.2, 0, the corresponding values of X are obtained: 0.2, 0.4 ... ... 3.

These particular values of X and of Y are shown on the graph (Fig. 5) by the points 1, 2, 3 ... ... 7 and 8.

There was then prepared a series of mixtures containing proportions of sulfur and tetramethylthiouram disulfide corresponding to those represented by these points.

These mixtures were then vulcanized and subjected to artificial aging tests.

From the point O' was drawn a line $O'Y'$ perpendicular to the straight line $Y = 1.5 - \frac{X.}{2}$

With these new coördinates $O'X'$ and $O'Y'$ were plotted as ordinates the values of the product $A \times C$ corresponding to the mixtures 1, 2 ... ... 8, vulcanized 10 minutes at 2 kilograms. There was thus obtained the curve A which shows that the best physical properties correspond to mixture 5, *viz.*, a mixture with 0.6 per cent sulfur and 1.8 per cent tetramethylthiouram disulfide.

On the ordinate the values of the product $A \times C$ for the Mixtures 1, 2 ... 8 after artificial aging for 10 days were then plotted. There was thus obtained curve B, which increases progressively from Mixture 1 to Mixture 8.

On this diagram there was then plotted, as shown on the dotted curve, the way in which the percentage loss of product AC varies for a 10-day heating in the oven from Mixture 1 to Mixture 8. This difference, which is equal to about 30 per cent for Mixture 1, becomes 43 per cent for Mixture 5, drops to only 29 per cent for Mixture 7, and to only 8 per cent for Mixture 8.

These tests show that mixtures vulcanized with very little sulfur, or even in the absence of sulfur and with large proportions of accelerator, age best under these conditions with a vulcanization of 10 minutes at 2 kilograms.

These experiments also show that for vulcanization at a given temperature and a given time there are proportions of sulfur and of accelerator for which the aging qualities of the vulcanized mixture are distinctly better than the aging obtained with other proportions. In particular, with tetramethylthiouram disulfide and diphenylguanidine it seems advantageous to use large proportions of accelerator.

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The Effect of Pigments in Rubber

F. Boiry

Certain pigments, mixed with rubber, change its physical properties when vulcanized. Wiegand,[1] in the first of his interesting publications, divided these pigments into two classes:

1. Inactive pigments, which have no effect on the physical properties of rubber (barium sulfate, lithopone, silica), and

2. Active pigments[2] (gas black, lamp black, zinc oxide) which improve the physical properties of rubber, increase the total resilient energy, and very often its tensile strength.

Since we proved in an earlier experiment that gas black, the most active of all pigments,[3] imparts to raw rubber a certain insolubility or, to be more exact, that mixtures containing a certain proportion of gas black (10 volumes of black per 100 of rubber) do not disaggregate in the ordinary rubber solvents, particularly in benzene hydrocarbons, it was decided to investigate whether other pigments possess this property, and if there is any relation between this property and the effect of pigments on the physical properties of vulcanized rubber.

Although these experiments are not complete and have not led to very definite conclusions, the results are of some interest for the information which they give about the effect of pigments, particularly since to our knowledge the only works on this subject are those of Le Blanc and Kröger[4] on blacks, and Depew on gas black[5] and ZnO.[6]

1. *Solubility of Unvulcanized Rubber Mixtures.*—Before examining the influence of various pigments, it might be well to review the behavior of raw rubber unmasticated or mixed with gas black when immersed in a solvent.

1*a*. *Unmasticated Rubber.*—Rubber is soluble in numerous liquids and as is known the longer it has been worked on the mixing rolls, the more easily it is dissolved. If thin strips of unmilled rubber are covered with toluene they swell greatly while absorbing the solvent. On progressive addition of solvent, the swelling continues, the swollen strips of rubber keep their shape and their general appearance, and do not unite with the adjoining strips. An excess of solvent brings about solution and after a relatively long time, which may exceed 3 or 4 days, a thick solution is formed, a heterogeneous magma, in which the strips saturated with solvent can still be recognized. The transformation of this solution into a more fluid solution by the addition of solvent and agitation is laborious.

If strips of unmasticated rubber are immersed in a great excess of solvent, they swell and float in the liquid, while preserving their shape, and this swollen rubber appears to be surrounded by a layer of a clearer solution hardly distinguishable from the solvent. The more concentrated the solution the more slowly does the rubber pass into solution. Finally, the skeleton of insoluble substances settles to the bottom of the receptacle.

When the rubber has been masticated, swollen rubber passes into solution much more rapidly. After several hours of contact with the solvent the strips of swollen rubber settle in a thick solution which spreads out over the bottom of the receptacle and which gives a clearer homogeneous solution by repeated agitation with the excess liquid.

1*b*. *Mixtures with Gas Black as a Basis.*—If strips of a mixture containing a certain proportion of gas black are immersed in a great excess of toluene or, if the latter is added progressively to the strips, no solution appears to take place. The mixture swells strongly, but the strips retain their shape and their individual character and do not unite at any time. However, the rubber dissolves, as can be proved by decantation and evaporation of the solvent. The strips which float in the liquid are surrounded (like those of unmasticated rubber) by a layer of solution, free from pigment, of which the thickness and index of refraction are different from those of the surrounding liquid, and which is held back very strongly by the black mixture.

In mixtures which are not too heavily loaded with black, there comes a time when the swollen mixture disaggregates, and the black, passing into suspension in the solvent, gives to the latter a brown color. With sufficient agitation of the liquid the rubber strips are broken into tiny fragments and disaggregation takes place a little more rapidly. In order for this disaggregation to take place there must be a considerable excess of solvent. Contrary to the case of unmasticated rubber, strips of the mixture containing black do not, after having attained their maximum swelling, unite upon addition of a slight excess of solvent. Some rubber passes into solution in the latter, but the strips suspended in this solution do not unite and do not disaggregate.[7]

The time required for the mixture to begin to disaggregate depends directly on the proportion of pigment but also on the condition of the rubber. A mixture milled to excess, either before or after the addition of the black, and a mixture immersed very soon after its preparation, disaggregate more quickly than a mixture not milled to excess or well rested.[8]

Mixtures with 5 volumes of black (for 100 volumes of rubber) begin to disaggregate after a few days' immersion. Part of the rubber passes into solution, some black passes into the liquid giving it a brown color, and the strips break into fragments.

After having been milled to excess, mixtures with 10 and even 20 volumes behave like mixtures with 5 volumes. Those which have undergone normal milling are not disaggregated after several months in toluene. By renewing the solvent frequently (in these experiments the solvent was decanted and replaced by fresh solvent every other day during the first month, then every week) mixtures with 10 volumes began to disaggregate after 2 to 3 months' immersion. Those containing 20 and 50 volumes or more of gas black appeared to be intact after 6 months. When separated from the solvent by decantation, the pieces of swollen rubber did not settle under their own weight, and they maintained their form very well. After drying they formed a black shiny film with a hardness which approached that of ebonite.

Table I gives the results of analysis of some of these mixtures.

Mixtures 1, 4, 5, and 6 were analyzed after 3 months in toluene; No. 1 then began to disaggregate; Nos. 2 and 3 were analyzed at the moment when disaggregation began. No. 1 was a mixture weighing 20 kilograms which was mixed on a factory scale and much less worked, *i. e.*, it was less "dead" than the other mixtures weighing 500 grams to 1 kilogram, which were prepared on a laboratory mill.

Mixture 1 disaggregated less rapidly than Mixture 2, which disaggregated more quickly one week after its preparation (No. 2) than after 3 months' standing (No. 3). Mixture 5, with 72 volumes, had been studied. A mixture with 10 volumes when first tested having (like Mixture 1) begun to disaggregate with this proportion, it appeared of interest to see how a mixture having this composition

TABLE I

No.	Composition of Original Mixture			Final Mixture			Rubber for 10 Volumes of Black		Rubber Which Passed into Solution (in % Rubber of Original Mixture)	Time of Beginning of Disaggregation	Remarks
	Rubber	Gas Black		Rubber	Gas Black		Original Mixture	Final			
		Weight	Volume		Weight	Volume					
1	100	18	10	100	130	72.2	100	13.9	86.1	After about 3 months	Mixture immersed 1 week after preparation
2	100	18	10	100	66	36.6	100	27.4	72.6	After about 2 months	Mixture immersed 1 week after preparation
3	100	18	10	100	75.6	42	100	23.8	76.2	After about $2^1/_2$ months	Same mixture as 2 immersed 3 months after preparation
4	100	36	20	100	79	43.9	50	22.8	54.4	Unchanged after 6 months	Mixture immersed 1 week after preparation
5	100	130	72	100	185	102.8	13.58	9.73	29.8	.....	.....
6	100	200	111	100	238	132.2	9.00	7.57	15.9	.....	.....

would behave. The solvent content was determined in Mixtures 2 and 3 before determining the black. It was considerable.

	2	3
Weight of toluene per 100 parts of the final mixture	3491	3637
Weight of toluene per 100 parts of rubber in this mixture	5798	6385

1*c*. *Mixtures Containing Other Pigments.*—The pigments which were tested included zinc oxide, litharge, light calcined magnesia, light magnesium carbonate, hydrated lime, Meudon white (whiting), lamp black, kaolin, lithopone, golden antimony sulfide (45 per cent $CaSO_4.2H_2O$, 17 per cent free S), crimson antimony, talc, silica (kieselguhr antimony trioxide). All these mixtures were made by working the rubber as little as possible.

aa. *Mixtures with 10 Volumes.*—The mixtures containing litharge, light calcined magnesia, and hydrated lime behaved like gas black mixtures. Immersed in toluene 1 week or 3 months after preparation, the other mixtures disintegrated at the end of a few hours.

bb. *Mixtures with 20 Volumes.*—The mixtures already mentioned and the mixture with magnesium carbonate did not disaggregate; the others disintegrated in toluene. Those with zinc oxide and lithopone disintegrated the most rapidly.

cc. *Mixtures with 50 Volumes.*—The mixture with lamp black did not disaggregate; the others disintegrated.

Table II gives the analysis of the mixtures which did not disintegrate at the moment when they began to disaggregate. In the case of gas black, the less the mixtures were worked and the longer the time before immersion, the slower was the disaggregation. Mixtures with light calcined magnesia kept their shape the best, in fact almost as well as those containing gas black.

It should be mentioned that in the case of calcined magnesia and magnesium carbonate, the higher the proportion of pigment the more insoluble were the mixtures. The case is different with hydrated lime and litharge. Is this a normal effect or is it to be explained by an anomaly resulting from external causes which were not recognized? This is a point which has not yet been explained. In those mixtures which disintegrate, the powder settles to the bottom of the receptacle where it forms an apparent skin with an appreciable cohesion. After solution of the rubber in a mixture containing 10 volumes of zinc oxide, the supernatant liquid was decanted, and the residual powder was washed 3 or 4 times by decantation. Analysis of this zinc oxide (No. 10 of Table II) shows that the rubber retained (perhaps mechanically) by the zinc oxide is only a trace.

Rubber Is Highly Absorbed by Certain Pigments

Depew[9] explains the insolubility of rubber mixed with gas black by the formation of a sort of semi-permeable membrane resulting from the flocculation of the pigment in the unvulcanized rubber, where the micelles diffuse very slowly through this membrane.

This explanation does not seem to account exactly for the facts which have been observed. The rubber is not insoluble, but at least up to a certain limit it dissolves progressively, though more difficultly than when it has not been mixed with pigment.

It is more probably a case of strong, but reversible, adsorption of the rubber by certain pigments. The layer of dissolved pure rubber which adheres very strongly to the swollen mixture shows to what extent the rubber, in spite of its affinity for the solvent in which it is immersed, is strongly retained by the pigment which is nevertheless very far removed. As a result of this adsorption, solution of the

TABLE II

	Original Mixture			Final Mixture			Rubber per 10 Volumes of Pigment		Dissolved Rubber (in % of Rubber in Original Mixture)	Time of Immersion Required to Produce Disaggregation	Observations
		Pigment			Pigment						
	Rubber	By Weight	By Volume	Rubber	By Weight	By Volume	Original Mixture	Final Mixture			
					Litharge						
1	100	92.5	10	100	288	31.1	100	32.1	57.9	52 days	Immersed 1 week after preparation
2	100	92.5	10	100	229	24.7	100	40.5	59.5	57 days	Same mixture as 1. Immersed 3 months after preparation
3	100	185	20	100	850	91.9	50	10.9	78.2	13 days	Immersed 4 weeks after preparation
					Light Calcined Magnesia						
4	100	33	10	100	112	33.9	100	29.5	70.5	Unchanged after 52 days	Immersed 1 week after preparation
5	100	66	20	100	114	34.5	50	29	42	Unchanged after 3 months	.....
6	100	66	20	100	140	42.4	50	23.3	53.4	94 days	Same mixture as 5, but worked an extra 40 minutes
					Hydrated Lime						
7	100	30	10	100	141	47	100	21.3	78.7	63 days	Immersed 1 week after preparation
8	100	60	20	100	211	70.3	50	14.2	71.6	17 days	.....
					Magnesium Carbonate						
9	100	55	20	100	218	82	50	12.2	75.6	42 days	.....
					Zinc Oxide						
10	100	55	10	100	2930	537.7	100	1.86	98.14	Disintegrated after 3 hours	.....

rubber becomes very slow, and perhaps a state of equilibrium is established between the solvent and the pigment.

Moreover, as has been seen earlier, rubber, without dissolving, can absorb a large quantity of solvent, in fact much more than that necessary to carry the swollen rubber into solution. The influence of the pigment particles on the micelles farthest away, and which are moreover isolated by a greater and greater thickness of solvent, becomes more and more feeble, and there comes a time when this influence is not great enough to maintain the cohesion of a rubber supersaturated with solvent. At this moment disaggregation takes place.

In the mixtures most heavily loaded with pigment the particles are closer together, and their influence is not extended over such a large area as in mixtures which are not so rich in pigment. The thickness of the rubber between the particles is less, and consequently the swelling is less pronounced. Moreover the effect of the pigment particles on the rubber micelles in loaded mixtures is very intense, even at the maximum swelling. As a result, the rubber passes into solution very slowly, the cohesion of the mixture is not destroyed by the action of the solvent, and disaggregation does not take place, or takes place only after a very long time.

In lightly loaded mixtures, on the contrary, the micelles farthest away from the particles of powder are no longer attracted by the latter as soon as the mixture begins to be greatly swollen, and disaggregation takes place rapidly.

The more rubber is masticated, the more readily does it pass into solution, and this explains why in mixtures which have been milled excessively disaggregation proceeds more rapidly and affects a higher proportion of the rubber than in mixtures which have been milled to only a moderate degree.[10] It seems that the particles of rubber remain surrounded by a film of rubber[11] when disaggregation takes place.

Pigments which seem to form with rubber a relatively stable adsorption compound may be ranked in the following decreasing order—gas black, light calcined magnesia, litharge, hydrated lime, magnesium carbonate, and, finally, lamp black.

The intensity of the adsorption depends on the following two factors: (1) a *capacity factor* represented by the specific surface of the phases, and (2) an *intensity factor*, the nature of which is little understood. According to some authors[12] non-polar substances should be good adsorbents of non-polar compounds, whereas polar substances should adsorb particularly polar compounds. If this were true, gas black and lamp black, which have the largest specific surface of all the pigments and which are in addition the only two non-polar pigments, should be the best absorbents of rubber.[13] This is true of gas black, but not of lamp black. The influence of these pigments on the solubility of rubber is probably proportional to their relative specific surfaces; lamp black is much inferior to the coarser pigments like magnesia, litharge, etc. These have a much more pronounced influence on the solubility of rubber, as would be expected from their degree of fineness.

These pigments are all strong bases, and one of them is a basic salt. Since these substances react with the fatty acids in the rubber resin, the soaps which are formed may have an influence on the solubility of raw rubber. This influence is, however, insufficient at least to explain the phenomena observed, for mixtures of 2 to 3 volumes of these pigments dissolve like rubber containing no pigment.

Perhaps complex salts are formed in which the acid radical saturated by the metal base adheres strongly to the pigment particles, the hydrocarbon chain being dissolved in the rubber. These fatty acids would in this way form a very strong bond between the rubber and the pigment.

This action can be better explained by the electric charge of the particles, which

plays a very important part in the reënforcement of the rubber, but about which up to the present, nothing, it might be said, has been published.[14]

According to Knoblauch[15] substances which are neither very acid nor very basic are changed negatively by bases and positively by acids. Inorganic salts do not give any definite result.

Under the action of distinctly basic substances like magnesia and its carbonate, lime and litharge, rubber would take a highly negative charge, whereas particles of these pigments would be charged positively.

With other pigments which are neutral salts (barium sulfate, silicates) oxides of weak basicity or weak acidity (zinc oxide, silica), the charge on the rubber would be weak.

In his generalization of the Gibbs' theorem, Wo. Ostwald[16] says: "Adsorption takes place when there is a difference in the potential energy of a surface which can be reduced by a change in the concentration of dispersed substances on this surface." Accordingly, a strong adsorption of rubber by basic substances should be expected, because there is a great difference in the electric potential between these substances and rubber, whereas no such difference in potential is found with other pigments. This explains the absence of a marked adsorption. This very strong union of rubber and basic pigments is a phenomenon analogous to the adsorption and mutual precipitation of two colloids of the opposite sign.

This influence of inactive and active pigments on raw rubbers can also be compared to that of certain pigments on oils, particularly linseed oil. Meudon white mixed with linseed oil adsorbs this liquid strongly and forms a plastic paste; *i. e.*, glazier's putty. Lithopone, on the contrary, under the same conditions is well wetted by linseed oil, but it does not adsorb it. This mixture remains liquid. In this latter case the dispersion medium is the oil, and lithopone is the dispersed phase. In glazier's putty, the properties of which resemble those of jellies, the liquid is the dispersed phase and Meudon white is the dispersion medium. In rubber mixtures, inactive pigments are the dispersed phase, and rubber the dispersion medium, at least for mixtures not overloaded (below 50 volumes).

TABLE III

Pigments	Mixtures with 10 Volumes of Pigment per 100 of Rubber: Tensile Strength in Kg. per Sq. Mm.	Mixtures with 10 Volumes of Pigment per 100 of Rubber: Total Resilient Energy	Maximum Load at Rupture: In Kg. per Sq. Mm. Cross-Section	Maximum Load at Rupture: Volume of Pigment per 100 of Rubber	Total Resilient Energy: Maximum	Total Resilient Energy: Volume of Pigment per 100 of Rubber	Average Diameter of Pigment Particles
Base mixture (rubber 90—sulfur 10)	1.650	100					
Gas black	1.910	130	2.800	25	182	25	Submicroscopic
Light calcined magnesia	2.080	133	Not determined				0.6 to 1μ
Magnesium carbonate	2.140	136	2.140	10	181	20	0.8 to 1μ
Litharge	2.000	112	Not determined				1 to 2μ. Many particles large up to 30μ
Hydrated lime	1.600	102	Not determined				About 1μ
Lamp black	1.900	126	2.010	15	133	15	Submicroscopic
Zinc oxide	1.720	114	1.820	15	120	15	0.5 to 0.6μ

With active pigments, as a result of adsorption of the rubber by the pigment, even for a relatively weak concentration (20 volumes of pigment) there will be a

reversion of the phases, the pigment constituting the dispersion medium and rubber the dispersed phase. Perhaps the manner of behavior of mixtures with respect to solvents is changed when this reversion of phases takes place.

Is There a Relation between the Effect of Pigments on the Solubility of Raw Rubber and Their Effect on the Physical Properties of Vulcanized Rubber?

It seems very probable that there is a relation between the effect of pigments on the solubility of raw rubber and their effect on the physical properties of vulcanized rubber. On the one hand, inactive pigments have no appreciable influence on the solubility of raw rubber. On the other hand, with the exception of zinc oxide all active pigments give mixtures which do not disaggregate in solvents. The forces which oppose the separation of the ingredients in the mixture under a tractive force are evidently the same forces which oppose this separation under the influence of solvents.

Although in mixtures which are not heavily loaded there is a close relation between the two effects, this is no longer true when the proportion of pigment is increased beyond a certain limit (about 25 volumes of pigment for 100 of rubber).

The resistance of these mixtures to solvents increases with the percentage of pigment, whereas their resistance to traction diminishes.

This is without doubt due to the fact that there is no longer enough rubber to envelop all the particles of pigment. The latter form agglomerates which behave like individual particles toward the solvent, but which set up points of less resistance to traction where rupture starts.

Table III shows the loads at rupture and the total resilient energy for mixtures of 10 volumes of pigment per 100 of rubber. The maximum value of this load at rupture and of the resilient energy for each pigment with the volume of the latter correspond to this maximum and the average dimension of the particles of pigment.

According to Wiegand[17] two factors play a part in the reënforcement of rubber by pigments,[18] first a capacity factor, the specific surface of the pigment, and second, an intensity factor, the interfacial tension between rubber and pigment.

Table III shows that for gas black, magnesium carbonate, and calcined magnesia there is a close relation between the effect on the solubility of raw rubber and the reënforcing power. However, as has already been said, these last two pigments have, in comparison with lamp black, zinc oxide, and perhaps even gas black, a much more pronounced action than would be foreseen from the size of their particles, *i. e.*, their specific surface. Accordingly, the intensity factor for these pigments is much greater than for the other pigments.

Litharge does not reënforce rubber as much as would be expected from its action on raw rubber. This is due without doubt to the large dimension of some of the particles and to its small specific surface, and perhaps also to the formation during vulcanization of lead sulfide and lead sulfate,[19] which changes either the electric charge of the particles or the pigment system: lead soap–rubber.[20]

Except for an intensity factor which is less than that of magnesia and magnesium carbonate, lamp black would behave in the normal manner, at least in comparison with gas black, as a reënforcing agent and in its action on raw rubber. However, two pigments, zinc oxide and hydrated lime, have the opposite effect on these two properties.

According to Wiegand and numerous others, zinc oxide in relation to its specific surface occupies an abnormal position as a reënforcing agent. It should not, according to these authors, be more effective than lithopone since the dimensions of the particles of the two pigments are of the same order of magnitude.

On the contrary, it does not have the same influence on the solubility of raw rubber that lithopone has. In this respect, it would appear to occupy a normal position. Therefore, during vulcanization it should develop its reënforcing effect. Zinc oxide, which is required for the action of accelerators, reacts chemically during vulcanization, and it is these reactions which would bring about its reënforcing action, which is moreover rather moderate.

In the case of hydrated lime, its almost negligible effect on vulcanized rubber, in comparison with its very pronounced action on the solubility of raw rubber, must be the result of chemical reactions or physical modifications during vulcanization.

Can the Effect of Pigments Be Modified?

Wiegand[21] has raised the question if it is possible to change the electric charge of pigments. With this question we, too, have concerned ourselves. If the reënforcing action of pigments is especially pronounced in the case of bases which charge rubber negatively, is it possible to modify the surface of other pigments so as to obtain a difference of potential and a greater adsorption between them and the rubber?[22]

With this in mind we tried to form two adsorption compounds by treating electronegative pigments (kaolin, lamp black, silica, etc.), with, first, weak alkaline solutions, second, gaseous ammonia, and third, basic dyes. Up to the present time only the first procedure has given definite results. However, it is possible that the improvement found is simply the result of an increase in the degree of division of the pigments.

Remarks

Certain phenomena of practical importance depend upon this adsorption of rubber by certain pigments.

1. Mixtures for cements containing gas black, litharge, etc., where the addition of the powders is made on a mixing mill, are more difficult to dissolve than those containing zinc oxide or other active pigments.
2. Cements made by adding the pigment in the churn are less viscous and less "nervy" for a given solvent and working than those where the pigment has been added on the mixing mill.
3. Adsorption and perhaps reversion of phases is one of the causes of scorching of mixes on the mill. This phenomenon appears to be most frequently a result of the beginning of vulcanization in the presence of sulfur and of accelerators. However, the same phenomenon has been observed in a mixture heavily loaded with magnesium carbonate on a very hot mixing mill, and Goodwin and Park[23] have described a similar phenomenon in mixtures very heavily loaded with gas black. It might be mentioned that active pigments are, according to Hurlston,[24] those pigments which diminish the plasticity of rubber.

Conclusions

1. Gas black, light calcined magnesia, litharge, hydrated lime, and, to a lesser degree, lamp black give mixtures which do not disintegrate in benzene hydrocarbons. These mixtures disaggregate only after prolonged immersion in an excess of solvent, and the less pigment they contain and the less disaggregated the rubber, as a result of the mechanical working, the longer is this time.

The other pigments with rubber form mixtures which disaggregate very rapidly, and from which the rubber dissolves very rapidly.

2. This effect of pigments of the first group is a result of adsorption of the rubber by the pigment particles.

3. In the case of gas black and lamp black, this adsorption phenomenon depends chiefly upon the very great specific surface of these pigments. With magnesia and magnesium carbonate, with hydrated lime, and with litharge it depends chiefly upon a difference in electric potential between the particles of pigment and the rubber.

4. There is a relation between the influence of the pigments on the solubility of raw rubber and their reënforcing effect on rubber after vulcanization. Gas black, magnesium carbonate, and calcined magnesium are the most active in both these respects. The relation is clearly defined in the case of lamp black, less so with litharge, and much less so with zinc oxide and with hydrated lime. The differences in the behavior of these last pigments are apparently due to chemical reactions which take place during vulcanization.

5. Tests carried out to modify the properties of these pigments have not up to the present time given definite results.

References

[1] Wiegand, *J. Ind. Eng. Chem.*, **13**, 118 (1921).

[2] In this paper it will be necessary to use the expression *active pigment* in the sense given by Wiegand "active on the physical properties of vulcanized rubber" and not from the point of view of "chemical activity."

[3] Boiry, *Rev. gén. Caoutchouc*, **3**, No 24, 12; No. 25, 11 (1926).

[4] Le Blanc, Kröger and Klotz, *Kolloidchem. Beihefte*, **20**, 356 (1925).

[5] Depew, *J. Ind. Eng. Chem.*, **11**, 1027 (1919).

[6] Twiss has also described the insolubility of mixtures of black. *J. Soc. Chem. Ind.*, **44**, 106T (1925). More recently Blow (*Trans. Inst. Rubber Industry*, **5**, 417 (1930)) called attention to the same fact and found an increase in viscosity of solutions of mixtures containing gas black.

[7] For the insolubility of black mixtures and the extraction of rubber from these mixtures by benzene, see Goodwin and Park, *Ind. Eng. Chem.*, **20**, 621 (1928).

[8] Depew, see note 5.

[9] Depew, see note 5.

[10] Le Blanc, Kröger and Klotz, *loc. cit.*, p. 380; Goodwin and Park, *loc. cit.*

[11] According to Carson and Sebrell, *Ind. Eng. Chem.*, **21**, 914 (1929), it is impossible to separate completely gas black from a rubber cement.

[12] Slater, *J. Soc. Chem. Ind.*, **44**, 161 (1925).

[13] It did not appear necessary in explaining the action of gas black on rubber to resort to the influence of stearic acid (see, for example, Blake, *Ind. Eng. Chem.*, **20**, 1084 (1928)). Moreover, Parkinson (*Trans. Inst. Rubber Industry*, **5**, 282 (1930)) proved that rubber extracted with acetone behaves toward black like untreated rubber.

[14] In the "Encyclopédie de Caoutchouc," Paris, **1929**, I have already mentioned, as a result of the work in the present paper, the importance of the electric charge of the particles, which has already been referred to in several papers (Wiegand, *India Rubber J.*, **73**, 34 (1927)).

[15] *Z. physiol. Chem.*, **39**, 225 (1902).

[16] Wo. Ostwald, "Grundriss der Kolloid-Chemie," Dresden **1909**, 1st Ed., page 434.

[17] Wiegand, *loc. cit.*

[18] These factors are the same as those which govern the phenomena of adsorption.

[19] Stevens, *J. Soc. Chem. Ind.*, **34**, 524 (1915).

[20] Depew, *loc. cit.*, has proved that zinc oxide, treated by sulfur trioxide, with formation on the surface of zinc sulfate, gives mixtures which can be dissolved more easily than those with untreated zinc oxide. The formation of lead sulfate would have an analogous effect here.

[21] *India Rubber J.*, **73**, 34 (1927).

[22] Such a change takes place during vulcanization with zinc oxide, and in the inverse sense with lime and litharge.

[23] *Loc. cit.*

[24] Hurlston, *Trans. Inst. Rubber Industry*, **2**, 267 (1926).

[From the Transactions of the Institution of the Rubber Industry, Vol. 7, No. 3, pages 209–227, October, 1931.]

Hysteresis and Reinforcement

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The object of this investigation was to examine the relationships existing between the work of extension (resilient energy) of vulcanized rubber and work of retraction and hysteresis loss, respectively, and to examine the effect of pigmen-

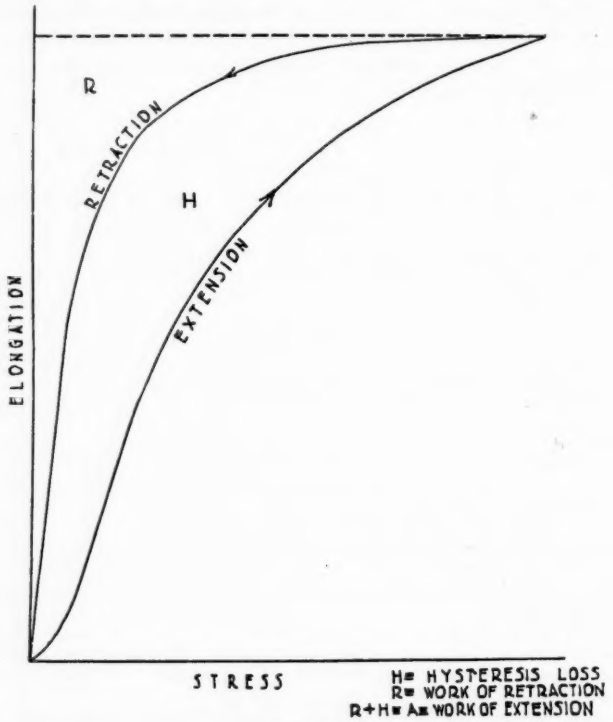

Figure 1

tation on these quantities. An attempt has been made to show that the increase in work of extension associated with reinforcement by fillers is largely due to frictional losses in the vulcanized product.

On extension of a sample of vulcanized rubber, the familiar stress-strain curve is obtained. When the rubber retracts the curve of retraction is nearer the strain axis (see Fig. 1). This effect is known as hysteresis. The work of extension is represented by the area A between the elongation axis and the stress-strain curve, the work of retraction R by the area between the retraction curve and the elongation axis, and the hysteresis loss H is therefore proportional to the area between the extension curve and the retraction curve.

If a sample of rubber be so slowly extended that no temperature change occurs, the work done in extension appears in three forms: (1) the potential energy (*P.E.*) due to elastic deformation; (2) as heat developed by internal friction (F_1), and (3) as reversible heat associated with the Joule effect (Q).

Hence:

$$\text{Area } A = P.E. + F_1 + Q.$$

On retraction, the potential energy is expended in doing the work represented by area R, and at the same time produces frictional heat (F_2). The potential energy is virtually increased by the absorption of the reversible heat Q.

Hence:

$$\text{Area } R = P.E. - F_2 + Q.$$
$$\therefore A - R = H = F_1 + F_2.$$

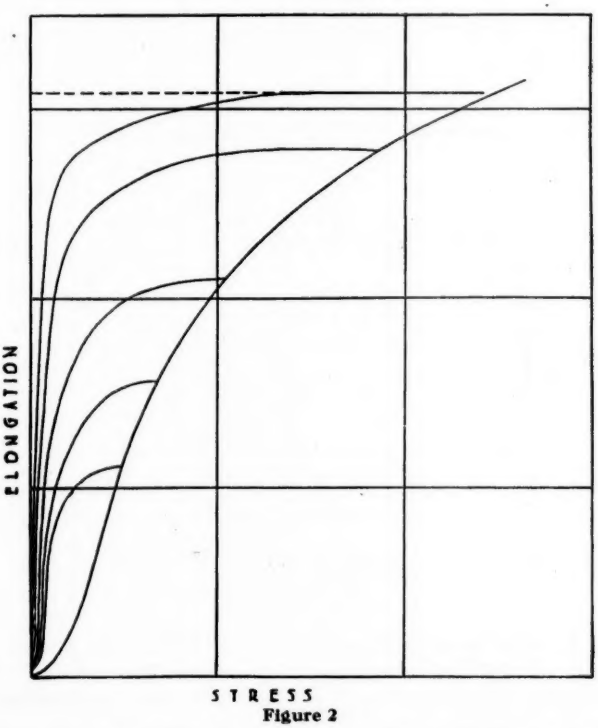

Figure 2

For the purposes of this investigation it is sufficient to assume that $F_1 = F_2$; *i. e.*, the frictional heat on extension is equal to that on retraction, and the hysteresis loss is approximately equivalent to twice the frictional heat.

Experimental

The base mix employed for the experimental work contained pale crepe rubber, 100 parts, zinc oxide, 5 parts; diphenylguanidine, 1.5 parts; and sulfur, 3 parts.

Diphenylguanidine was employed in virtue of its curing characteristics, which obviate the effects of small variations in time of vulcanization.

The high percentage was used to minimize the effects of fillers on the rate of vulcanization.

The fillers employed were standard grades of carbon black, zinc oxide (Red Seal and White Seal), china clay, and whiting. Dawson (*Trans. Inst. Rubber Industry*, **2**, 92 (1926)), Twiss (*India Rubber J.*, **65**, 607 (1923) *et seq.*), and Dawson and Hartshorne (*Trans. Inst. Rubber Industry*, **5**, 48 (1929)) have shown that the size and shape of filler particles play an important role in determining the behavior of compounded vulcanized rubber.

During heavy compounding, further strenuous mastication unavoidably occurs. To minimize such an effect, fillers corresponding to 50 volumes' loading were incorporated with rubber to form master batches, from which portions were taken and mixed with the required quantity of masticated rubber. The accelerator was then added as a master-batch, followed by the zinc oxide and sulfur. The stocks were allowed to stand for 48 hours before vulcanization.

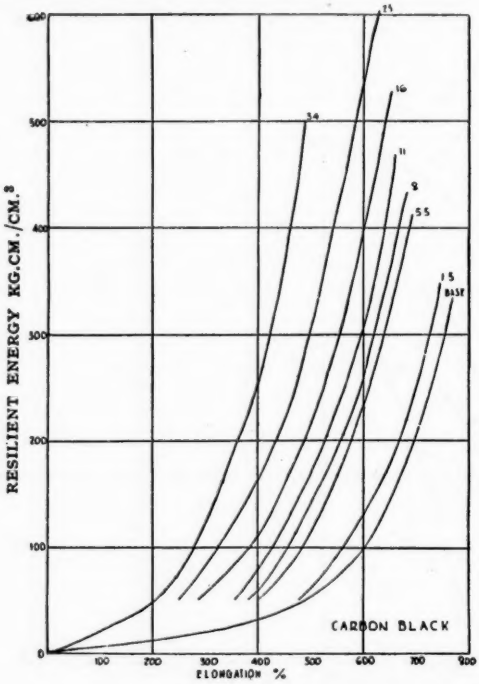

Figure 3

The properties of the different mixes were examined after they had been vulcanized to their optimum tensile strengths. To determine this, five different cures were made for each mix, and ten Schopper rings cut for tensile tests at each cure. The stocks for examination were then vulcanized to the optimum cures in a daylight press at a steam pressure of 40 lbs. per square inch, between tinned iron plates, 20 discs of each mix being vulcanized.

It has been shown by Vogt (*India Rubber J.*, **64**, 558 (1922)), using a Shields rotary machine, that the extent of the hysteresis loss is conditioned by the speed of the cycle of deformation and release. It was therefore decided to make all determinations so slowly that the temperature of the specimen under test remained constant. Ring samples were then stretched and released on the Schopper ma-

chine by increasing the load at such a rate that the velocity of extension remained constant at 600 per cent per minute, the velocity of retraction being about the same. After extending successive rings by stresses of 10, 20, 30, 40 kg., etc. (until as near the breaking point as possible), the pawls of the machine were re-

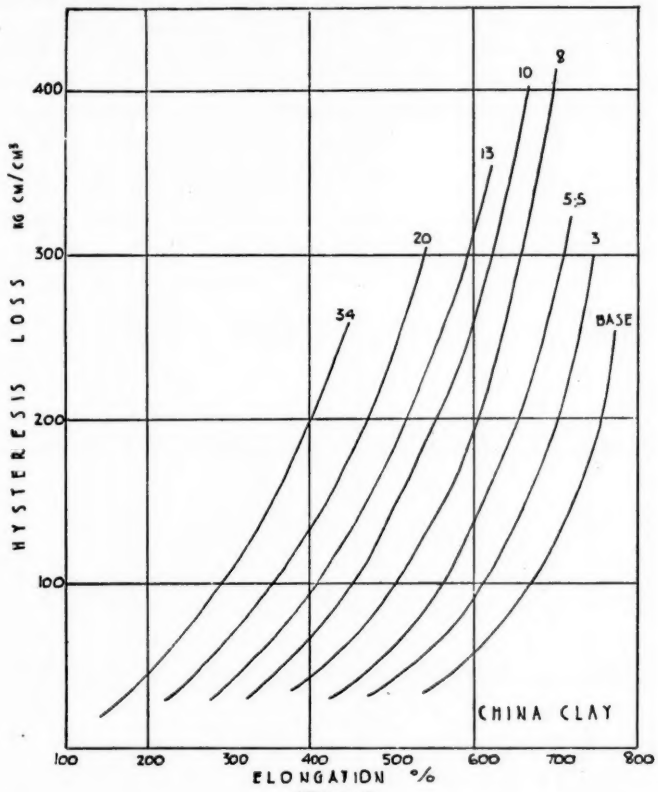

Figure 4

leased and the samples allowed to retract, readings being taken at intervals of 2 kg. Fresh rings were employed for each experiment, and one hysteresis loop only was recorded per ring. It was found more convenient to work to definite stresses than definite elongations. The type of curve obtained is shown in Fig. 2.

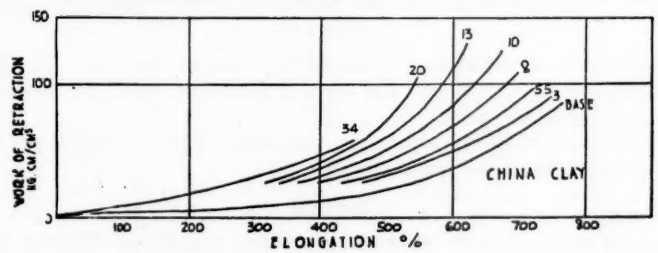

Figure 5

The areas R, A, and H (see Fig. 1) were determined with a planimeter and multiplied by the factor required to convert the values to energy units.

From the values obtained, curves were drawn connecting the elongation with the resilient energy (work of extension), hysteresis loss, and work of retraction, respectively, for the different mixes (see Figs. 3, 4, and 5). The relationships existing between the resilient energy, hysteresis loss, and work of retraction were also plotted. The work of retraction was found to vary directly with the resilient energy (see Fig. 6). This justified extrapolating the curves relating work of retraction

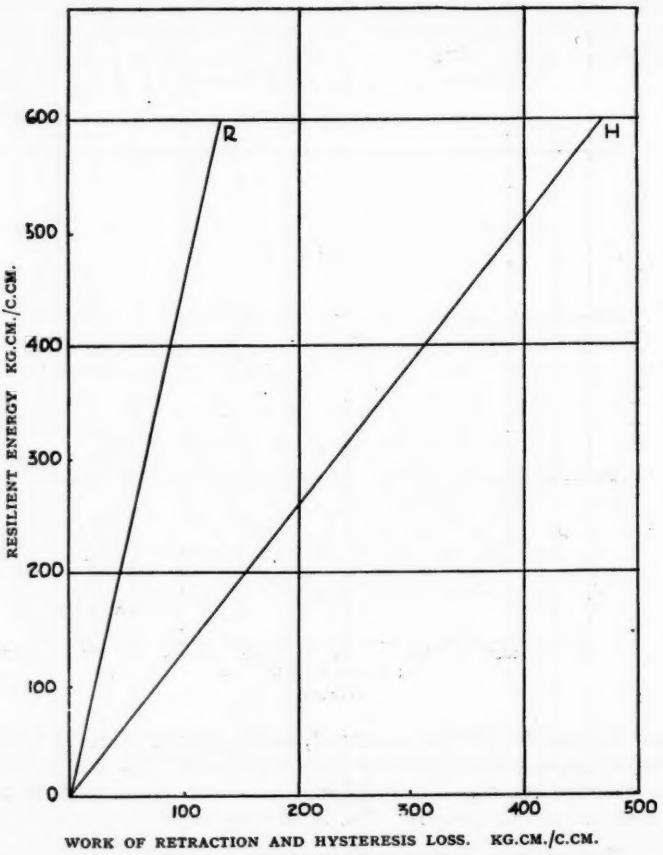

Figure 6

with elongation to the breaking point of the sample (see Fig. 5). Thus the ultimate values of hysteresis loss and work of retraction from the breaking point were obtained for all the mixes.

These values were then plotted against the volume loading of filler per 100 parts of rubber in each vulcanized sample (see Fig. 7).

Results

The results obtained with vulcanized rubbers containing different fillers are given in Tables I to V. The extrapolated energy values are recorded in Table VI.

TABLE I

	Base Mix						1.3 Vols. Carbon Black					
Stress, kg./cm.^{2}	45	83	131	155	180		49	89	126	150	164	185
Elongation, per cent	544	624	695	728	770		525	596	658	690	720	750
Work to extend, kg. cm./cm.^{3}	61.6	108	179.5	222.5	336		65.5	118.3	177.6	229.7	269	336
Hysteresis loss, kg. cm./cm.^{3}	34.5	69	119.5	154.4	256		37.6	73.6	121.2	162.8	198	260
Work obtained, kg. cm./cm.^{3}	27.1	39	60.0	68.1	80		27.9	44.7	56.4	66.9	71	76
	5.5 Vols. Carbon Black						8 Vols. Carbon Black					
Stress, kg./cm.^{2}	44	80	120	163	179	220	43	81	126	163	205	240
Elongation, per cent	400	505	546	615	654	703	384	470	553	605	657	690
Work to extend, kg. cm./cm.^{3}	50	114.1	167.3	259.6	318	409.6	47.4	101.6	190.9	266.5	358.9	428.8
Hysteresis loss, kg. cm./cm.^{3}	30.7	80.3	117.9	198.1	246.1	320	29.3	76.1	144.2	208.6	276	336
Work obtained, kg. cm./cm.^{3}	19.3	33.8	49.4	61.5	71.9	89.6	18.1	25.5	46.7	57.9	82.9	92.8
	11 Vols. Carbon Black						16 Vols. Carbon Black					
Stress, kg./cm.^{2}	40	81	126	163	205	250	39	78	117	209	234	255
Elongation, per cent	349	438	528	570	630	660	283	403	553	617	640	650
Work to extend, kg. cm./cm.^{3}	44.4	100.6	175.7	259.7	361.9	459.2	43.8	109	287.8	432.1	480.8	532.8
Hysteresis loss, kg. cm./cm.^{3}	24	66.2	135.6	198.6	281.6	364	26.4	74.1	222	332.4	371.5	420
Work obtained, kg. cm./cm.^{3}	20.4	34.4	40.1	61.1	80.3	95.2	17.4	34.9	65.8	99.7	109.3	112.8
	23 Vols. Carbon Black						34 Vols. Carbon Black					
Stress, kg./cm.^{2}	40	81	105	153	214	282	39	78	115	153	198	240
Elongation, per cent	238	298	394	480	576	640	166	251	310	377	424	500
Work to extend, kg. cm./cm.^{3}	45.8	99.7	152.8	256.8	442.4	600	29.8	79.7	144.7	229.2	323.2	496
Hysteresis loss, kg. cm./cm.^{3}	27.5	69.1	109	205	360	464	20.4	63	116.2	179.8	259.3	406.4
Work obtained, kg. cm./cm.^{3}	18.3	30.6	43.8	51.8	82.4	136	9.4	16.7	28.5	49.4	63.9	89.6

TABLE II

3 Vols. China Clay

Stress, kg./cm.^{2}	40	81	122	148	163	192
Elongation, per cent	483	583	642	671	700	740
Work to extend, kg. cm./cm.^{3}	63.2	116	176.5	225.6	257	388
Hysteresis loss, kg. cm./cm.^{3}	28.8	74.1	122.5	166.8	193.8	300
Work obtained, kg. cm./cm.^{3}	34.4	41.9	54	58.8	63.2	88

5.5 Vols. China Clay

Stress, kg./cm.^{2}	40	78	117	161	201	220
Elongation, per cent	420	519	585	649	698	720
Work to extend, kg. cm./cm.^{3}	55.6	109.2	177.8	262.3	349.3	416
Hysteresis loss, kg. cm./cm.^{3}	31.4	74	126.8	197.5	269.8	328
Work obtained, kg. cm./cm.^{3}	24.2	35.2	51	64.8	79.5	88

8 Vols. China Clay

Stress, kg./cm.^{2}	44	78	124	161	209	220
Elongation, per cent	384	480	563	623	670	690
Work to extend, kg. cm./cm.^{3}	58.9	113.9	197.3	295.8	381.8	512
Hysteresis loss, kg. cm./cm.^{3}	34.9	78.6	148.2	214.7	296.3	412
Work obtained, kg. cm./cm.^{3}	24	35.3	49.1	81.1	85.5	100

10 Vols. China Clay

Stress, kg./cm.^{2}	39	75	120	157	203	260
Elongation, per cent	318	422	492	542	604	670
Work to extend, kg. cm./cm.^{3}	45.8	100	180	250.7	350.5	524
Hysteresis loss, kg. cm./cm.^{3}	27.2	69.5	127.3	189	264.1	404
Work obtained, kg. cm./cm.^{3}	18.6	30.5	52.7	61.7	86.4	120

13 Vols. China Clay

Stress, kg./cm.^{2}	40	78	118	157	210	250
Elongation, per cent	275	386	452	507	548	615
Work to extend, kg. cm./cm.^{3}	42.4	106.9	172.9	247.1	336	484
Hysteresis loss, kg. cm./cm.^{3}	27.5	79.2	134.2	193.6	262.6	356
Work obtained, kg. cm./cm.^{3}	14.9	27.7	38.7	53.5	73.4	128

20 Vols. China Clay

Stress, kg./cm.^{2}	39	75	113	165	195	220
Elongation, per cent	220	315	382	463	490	540
Work to extend, kg. cm./cm.^{3}	39.1	94.8	155.5	273.8	327.5	411.2
Hysteresis loss, kg. cm./cm.^{3}	28.1	74.2	122.2	220.3	259	304
Work obtained, kg. cm./cm.^{3}	11	20.6	33.3	53.5	68.5	107.2

34 Vols. China Clay

Stress, kg./cm.^{2}	40	75	113	156	179	190
Elongation, per cent	142	231	309	366	403	450
Work to extend, kg. cm./cm.^{3}	25.6	77.2	148	225	280	313.6
Hysteresis loss, kg. cm./cm.^{3}	16.6	59.5	121.8	181	230.7	260
Work obtained, kg. cm./cm.^{3}	9	17.7	26.2	44	49.3	53.6

TABLE III

	1.5 Vols. Zinc Oxide (Red Seal)						3 Vols. Zinc Oxide					
Stress, kg./cm.^{2}	39	78	114	124	139	200	39	81	114	161	187	205
Elongation, per cent	540	628	687	695	735	800	525	632	670	750	776	790
Work to extend, kg. cm./cm.^{3}	72.7	113	182.5	243.6		409	70.8	141.4	185	299.7	334.7	432
Hysteresis loss, kg. cm./cm.^{3}	30	66.8	109	139		284	39.1	82.3	117.7	208.1	233	312
Work obtained, kg. cm./cm.^{3}	42.7	46.2	73.5	104.6		125.0	31.7	59.1	67.3	91.6	101.7	120

	8 Vols. Zinc Oxide						10 Vols. Zinc Oxide				
Stress, kg./cm.^{2}	42	84	117	150	179	214	43	86	129	161	210
Elongation, per cent	432	560	640	662	707	730	435	547	625	660	710
Work to extend, kg. cm./cm.^{3}	68.8	135.1	207.7	254	333	504	73.7	152.5	228.2	288.7	552
Hysteresis loss, kg. cm./cm.^{3}	35.3	82.4	133	170	233.3	365	44.5	97.9	159.6	208.2	408
Work obtained, kg. cm./cm.^{3}	33.5	52.7	74.7	84	99.7	139	29.2	54.6	68.6	80.5	144

	13 Vols. Zinc Oxide						19 Vols. Zinc Oxide				
Stress, kg./cm.^{2}	40	82	124	167	190	210	39	84	134	178	182
Elongation, per cent	396	525	586	650	668	690	368	486	572	635	640
Work to extend, kg. cm./cm.^{3}	60.1	145.6	216.5	313.7	351.5	512	63.4	149.2	232.3	307.4	458
Hysteresis loss, kg. cm./cm.^{3}	37.8	104.3	155.8	233	255.6	380	37.9	96.2	171.2	237.4	350
Work obtained, kg. cm./cm.^{3}	22.3	41.3	60.7	80.7	95.9	132	25.5	53	61.1	70	108

	33 Vols. Zinc Oxide				
Stress, kg./cm.^{2}	42	81	104	124	153
Elongation, per cent	317	454	522	575	595
Work to extend, kg. cm./cm.^{3}	64.2	142.8	208.6	272.5	340
Hysteresis loss, kg. cm./cm.^{3}	43	104	154.9	208.7	250.4
Work obtained, kg. cm./cm.^{3}	21.2	38.8	53.7	63.8	89.6

TABLE IV

10 Vols. Whiting

Stress, kg./cm.^{2}	43	90	119	160	173	190
Elongation, per cent	428	543	592	643	658	680
Work to extend, kg. cm./cm.^{3}	76.1	147.2	191	266.4	299	360
Hysteresis loss, kg. cm./cm.^{3}	42.8	90.4	120.7	177.2	200.2	256
Work obtained, kg. cm./cm.^{3}	33.3	56.8	70.3	89.2	98.8	104

15 Vols. Whiting

Stress, kg./cm.^{2}	49	83	132	156	184	195
Elongation, per cent	450	512	588	642	660	670
Work to extend, kg. cm./cm.^{3}	77.3	144.3	226.2	306.2	343.9	365.6
Hysteresis loss, kg. cm./cm.^{3}	44.4	91.2	162.5	212.4	237.5	257.6
Work obtained, kg. cm./cm.^{3}	32.9	53.1	63.7	93.8	106.4	108

20 Vols. Whiting

Stress, kg./cm.^{2}	58	101	144	164	190
Elongation, per cent	441	510	585	615	640
Work to extend, kg. cm./cm.^{3}	104	160	249.5	291.4	352
Hysteresis loss, kg. cm./cm.^{3}	61.2	101.1	189.2	206.2	257
Work obtained, kg. cm./cm.^{3}	42.8	58.9	60.3	85.2	95

25 Vols. Whiting

Stress, kg./cm.^{2}	41	84	131	153	176	188
Elongation, per cent	340	478	560	585	600	615
Work to extend, kg. cm./cm.^{3}	76	169.2	266.6	295	334.2	358.4
Hysteresis loss, kg. cm./cm.^{3}	43.8	113.4	196.4	212.3	246.4	268
Work obtained, kg. cm./cm.^{3}	32.2	55.8	70.2	82.7	87.8	90.4

40 Vols. Whiting

Stress, kg./cm.^{2}	42	85	105	128	146
Elongation, per cent	250	418	462	507	520
Work to extend, kg. cm./cm.^{3}	69.5	160.4	199	260	288
Hysteresis loss, kg. cm./cm.^{3}	44	110.9	147.6	198.1	219.2
Work obtained, kg. cm./cm.^{3}	25.5	49.5	51.4	61.9	68.8

TABLE V

	5 Vols. Zinc Oxide (White Seal)						10 Vols. Zinc Oxide				
Stress, kg./cm.^{2}	43	86	129	172	190	214	43	86	129	173	210
Elongation, per cent	500	615	685	756	780	800	457	595	671	728	760
Work to extend, kg. cm./cm.^{3}	70	145	224	331	400	510	74	163	244	347	546
Hysteresis loss, kg. cm./cm.^{3}	42	95	150	238	304	400	43	114	178	242	386
Work obtained, kg. cm./cm.^{3}	28	50	74	93	96	110	31	49	66	105	160
	15 Vols. Zinc Oxide						25 Vols. Zinc Oxide				
Stress, kg./cm.^{2}	43	86	130	173	210		43	86	130	173	190
Elongation, per cent	450	560	638	683	705		400	490	568	645	655
Work to extend, kg. cm./cm.^{3}	80	149	222	308	443		67	144	240	338	416
Hysteresis loss, kg. cm./cm.^{3}	37	95	171	233	334		43	89	162	268	332
Work obtained, kg. cm./cm.^{3}	43	54	61	75	109		24	55	78	70	84
	40 Vols. Zinc Oxide										
Stress, kg./cm.^{2}	43	86	130	168	180						
Elongation, per cent	294	420	510	560	590						
Work to extend, kg. cm./cm.^{3}	53	128	232	314	383						
Hysteresis loss, kg. cm./cm.^{3}	32	98	174	233	290						
Work obtained, kg. cm./cm.^{3}	21	30	58	81	93						

TABLE VI

Volumes of Filler	T_B, Kilos/Cm.^{2}	E_B—%	A, Kg. Cm. per Cm.^{3}	H, Kg. Cm. per Cm.^{3}	R, Kg. Cm. per Cm.^{3}	Time of Cure, 40 Lbs./In.^{2}
Base mix	180	770	336	256	80	25 min.
1.5 vols. carbon black	185	750	336	260	76	25 min.
5.5 vols. carbon black	220	703	410	320	90	26 min.
8.0 vols. carbon black	240	690	429	336	93	27 min.
11.0 vols. carbon black	250	660	459	364	95	29 min.
16.0 vols. carbon black	255	650	533	420	113	32 min.
23.0 vols. carbon black	282	640	600	464	136	34 min.
34.0 vols. carbon black	240	500	496	406	90	37 min.
3.0 vols. China clay	192	740	388	300	88	24 min.
5.5 vols. China clay	220	720	416	328	88	23 min.
8.0 vols. China clay	220	690	512	412	100	22 min.
11.0 vols. China clay	260	670	524	404	120	22 min.
13.0 vols. China clay	250	615	484	356	128	21 min.
20.0 vols. China clay	220	540	411	304	107	20 min.
34.0 vols. China clay	190	450	314	260	54	19 min.
1.5 vols. zinc oxide (Red Seal)	200	800	410	284	126	24 min.
3.5 vols. zinc oxide	205	790	432	312	120	25 min.
8.0 vols. zinc oxide	214	730	504	365	139	27 min.
11.0 vols. zinc oxide	210	710	552	408	144	28 min.
13.0 vols. zinc oxide	210	690	512	380	132	30 min.
20.0 vols. zinc oxide	182	640	458	350	108	33 min.
34.0 vols. zinc oxide	153	595	340	250	90	37 min.
10.0 vols. whiting	190	680	360	256	104	27 min.
15.0 vols. whiting	195	670	365	258	108	30 min.
20.0 vols. whiting	190	635	352	259	95	32 min.
25.0 vols. whiting	188	615	358	268	90	35 min.
40.0 vols. whiting	146	520	288	219	69	40 min.
5.0 vols. zinc oxide (White Seal)	214	800	510	400	110	23 min.
10.0 vols. zinc oxide	210	760	546	386	160	21 min.
15.0 vols. zinc oxide	210	705	443	334	109	18 min.
25.0 vols. zinc oxide	190	655	416	332	84	16 min.
40.0 vols. zinc oxide	180	590	383	290	93	12 min.

Work of Extension

Wiegand (*Ind. Eng. Chem.*, **17,** 939 (1925)) considered the work of extension a criterion of the reinforcement of rubber by fillers. The investigations of Wiegand (*loc. cit.*), Lunn (*Trans. Inst. Rubber Industry*, **4,** 396 (1929)), and Blake (*Ind. Eng. Chem.*, **20,** 10, 84 (1928)) leave little doubt that the interfacial tension existing between the surface of the filler particles and the rubber plays the most important part in determining the value of a reinforcing pigment (see review by Cotton, *Trans. Inst. Rubber Industry*, **6,** 248 (1930)).

The curves (see Fig. 3) for the work of extension at different elongations with increasing volume loadings of fillers resemble those of Lunn (*loc. cit.*). The *A* curve of Wiegand (*loc. cit.*) is obtained when work of extension is plotted against volume of pigment per 100 volumes of rubber. The areas obtained from the results for the *A* function (representing reinforcing power) were greatest with 25 volumes of carbon black, 10 volumes of zinc oxide (both Red and White Seal),

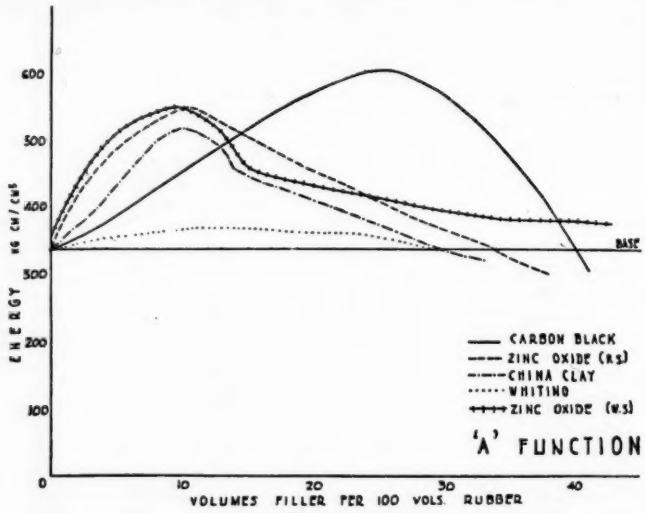

Figure 7

11 volumes of china clay, and 15 volumes of whiting, and decreased in that order. The zinc oxides did not differ appreciably in reinforcing power, the chief difference being that the White Seal accelerated the cure, while the Red Seal retarded it. The reinforcing action of the White Seal was maintained up to higher volume loadings.

Hysteresis Loss

Wiegand (*India Rubber World*, **63,** 425; **64,** 491 (1921)) expressed the view that the work done in stretching a sample of vulcanized rubber is connected with: (*a*) potential energy of strain; (*b*) reversible heat; and (*c*) frictional heat.

Though aware that much of the heat generated during extension of vulcanized rubber is associated with the Joule effect and is reabsorbed during contraction, he suggested that additional heat is developed by internal friction acting throughout the deformation cycle. This frictional heat is responsible for the continued rise in temperature of masses of rubber, such as are met in solid tires, under the action of repeated stresses.

When the rubber is extended slowly the reversible heat is dissipated. Wiegand confined his investigations to carbon black mixings, in which he regarded hysteresis loss as entirely associated with frictional forces, which would rise with increasing lateral compressions.

Whereas Wiegand states that hysteresis losses increase in proportion to the volume of filler present, it is found from the results tabulated above that the value of the hysteresis only increases to a point at which the greatest reinforcement occurs (as measured by resilient energy), and then decreases (see Figs. 7 and 8).

It was found that the increment in the resilient energy (*i. e.*, the reinforcement), due to the incorporation of fillers, is always greater than the corresponding increase in the hysteresis loss. This is demonstrated in Figs. 7 and 8, from which it will be observed that the *H* curve representing the hysteresis loss is always lower than the corresponding *A* curve. If it be assumed that hysteresis loss is due to frictional forces in the rubber, the greater portion of the work of extension must be due to internal friction. It is suggested that the slight increase in work of retraction

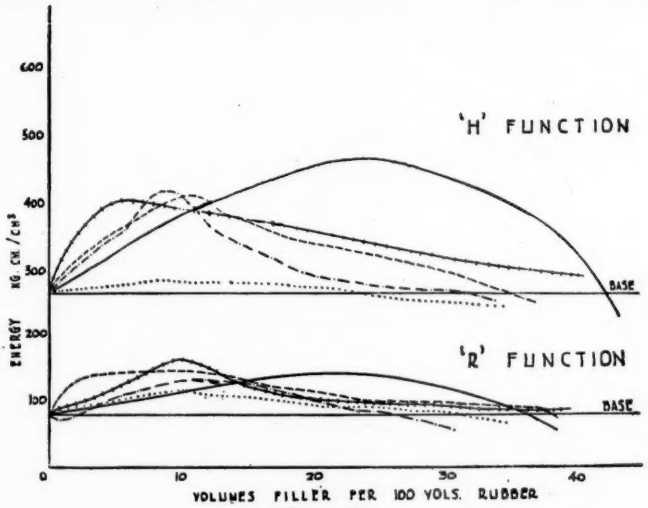

Figure 8

caused by reinforcement is derived from the surface energy of the particles, determined by the extent of wetting by the rubber. Hock (*Z. Electrochem. Angew. Phys. Chem.*, **34**, 662 (1928)) arrived at similar conclusions by thermodynamic methods.

Fillers increase resilient energy and hysteresis loss to a similar extent. Wiegand (*loc. cit.*) showed how the thermal properties of fillers affect the heat generated at the center of a large bulk of vulcanized rubber under stress, pointing out that while both carbon black and zinc oxide give greatly increased frictional heat, the latter gives superior results by virtue of its better conductivity and specific heat. According to Schippel, the formation of vacuoles in rubber compounded with inert fillers causes a partition of the energy used in extension; part going to distort the rubber phase and the remainder to tear the rubber from the particles. The relatively small surface of contact between rubber and fillers of large particle size may account for the low reinforcement obtained with these; and the consequent freedom of motion of the rubber phase probably results in lower hysteresis loss.

Work of Retraction

The work lost in stretching a reinforced rubber as distinct from that stored as potential energy of strain must be used in overcoming: (1) the forces of adhesion between rubber and that part of the filler wetted by the rubber, (2) the interfacial tension between the pigment and the rubber which resists any tendency toward increase in total surface area exposed between the rubber and the pigment, (3) the friction between flocculated particles of fillers incompletely wetted by the rubber, and (4) the friction between rubber particles undergoing reversible plastic flow around the filler particles.

That part of the hysteresis loss represented by items 3 and 4 will increase with compounding. On the other hand, the forces in 1 and 2 will only increase with compounding up to a point. Until this point is reached the work returned during retraction should also increase owing to re-formation of an interface. The *R* curves

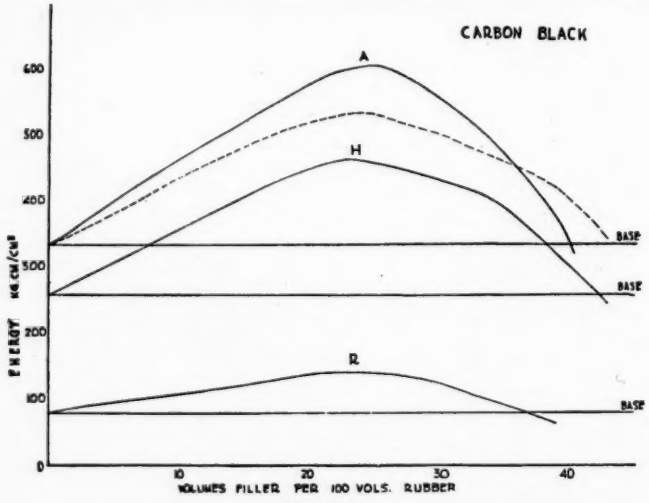

Figure 9

in Fig. 8 rise slightly with reinforcement before falling to the value given with the base mix.

A typical curve showing the relationship between work of retraction and elongation is given in Fig. 5. There was no tendency for curves representing rubbers differently loaded to superimpose, as suggested by Conover (*Ind. Eng. Chem.*, **22**, 891 (1929)). The greatest work of retraction was obtained with mixes which gave maximum reinforcement. Thus 25 volumes of carbon black, 10 volumes of zinc oxide (Red Seal and White Seal), 13 volumes of china clay, and 15 volumes of whiting, respectively, gave the maximum work of retraction. The work returned by vulcanized zinc oxide stocks was higher than that returned by other compounded rubbers, probably owing to the superior wetting of zinc oxide by rubber.

Conover concluded that the work of retraction from any given elongation is independent of the kind or proportion of pigment used. Hence the amount of energy released on retraction of any compounded rubber should be the same as would be returned from a pure gum mix strained to the same elongation. This is contrary to experience.

Discussion

From Fig. 1 it is seen that:

$$A = H + R$$

where

A = work of extension (resilient energy),
H = hysteresis loss,
R = work of retraction,
$\therefore R = A - H,$

whence if A increases at a greater rate than H, R will increase. This has been confirmed for reinforcing fillers.

Conover attributes reinforcement of rubber to increase in internal friction. What experiment proves to occur may be deduced by the following logical analysis of the deformation cycle:

In general,

$$A = H + R \quad \ldots\ldots (1)$$

For the base mix

$$A = H_B + R_B$$

If reinforcement occur, the values of A, H, and R will alter thus:

$$A \rightarrow A_B + \Delta A,\ H \rightarrow H_B + \Delta H,\ R \rightarrow R_B + \Delta R,$$

or substituting in (1)

$$A_B + \Delta A = H_B + \Delta H + R_B + \Delta R,$$

or

$$A_B - (R_B + H_B) + \Delta A = \Delta R + \Delta H,$$

or

$$\Delta A = \Delta R + \Delta H \quad \ldots\ldots (2)$$

The quantity ΔR is always positive for reinforcing fillers.

Conover, however, states that from any definite elongation, the work of retraction is the same irrespective of the proportion or nature of the filler; whence

$$\Delta R = O,$$

and therefore

$$\Delta A = \Delta H$$

or the increase in hysteresis loss is equivalent to the reinforcement; a conclusion which is contrary to the experimental evidence in this paper (see Figs. 7 and 8).

The results obtained confirm the conclusion reached by Dawson (*India Rubber J.*, **72,** 229 (1926)) that the finer the filler particles, the smaller is the ratio between work of retraction and work of extension. The suggestions of Hock (*loc. cit.*), Böstrom (*Kolloidchem. Beihefte* **26,** 10 (1928)), and Hartner (*Ibid.*, **30,** 83 (1929)), that the increase in the resilient energy due to fillers depends upon the free surface energy between the rubber and filler particles in addition to the work of friction, are in harmony with results obtained. Hock has suggested methods for evaluating the proportion of the reinforcement resulting from friction, and the proportion coming from the surface energy. He considers the latter to represent reinforcement of the ideal type. The results herein described suggest that the work returned on retraction from the breaking point may provide a measure of the reinforcement due to the surface energy between rubber and filler particles.

Summary and Conclusions

1. The relationships between work of extension, work of retraction, and hysteresis loss in vulcanized rubbers loaded with fillers have been examined.

2. The hysteresis loss in vulcanized rubber during a cycle of extension and retraction increases with amplitude to an extent comparable with the increase in work of extension.

3. If the work required to extend a vulcanized rubber to a given elongation be increased by compounding with fillers, the energy lost through hysteresis on slow retraction increases to a comparable extent. Hence reinforcement does not appreciably increase the ability of rubber to store energy.

4. With any rubber vulcanized to optimum tensile properties, hysteresis loss and work of retraction from any elongation are proportional to the work required to extend to that elongation. Therefore if the hysteresis loss during a given cycle be known, the work of retraction from the breaking point can be calculated.

5. The work of retraction from the ultimate breaking point of a vulcanized rubber increases slightly with reinforcement, and becomes greatest when reinforcement is at a maximum. This is thought to be a function of the rubber-filler interface.

6. No filler was found to lessen the work of retraction from the breaking point until the rubber was highly compounded.

7. It is suggested that the increased work required to rupture rubber that has been reinforced with fillers is mainly dissipated in overcoming consequent increased internal friction; a small quantity being converted to potential energy through strain of the filler-rubber interface.

[From Transactions of the Institution of the Rubber Industry, Vol. 7, No. 1, pages 48–55, June, 1931.]

A Short Note on the Tensile Testing of Rubber

M. Jones

The evaluation of rubber has centered largely around stress-strain phenomena, and the property of tensile strength is probably the one which has the most general application throughout the industry.

Rubber exhibits stress-strain properties quite different from the majority of substances, and peculiar difficulties are introduced during the determination of tensile strength. Although tentative standards have recently been issued by the American Chemical Society, there is no evidence that these are being strictly adhered to, and there is still need for a more rigid standardization of tensile-testing methods.

There are essentially two methods of tensile-testing:

(1) Using dumb-bell test-pieces with a Bureau of Standards machine, or a Scott type of machine; and

(2) Using ring test-pieces with a Schopper type of machine. It is generally supposed that higher tensile results are obtained by the former method. Recently, occasion has occurred to make a comparison between both types and to study the effect of certain factors upon each method.

For the Bureau of Standards machine, standard size dumb-bells were used. (Total length 6 in., length of constricted center portion 2 in., width of ends 1 in., and width of constricted portion $^1/_4$ in.) The jaws of this machine are capable of moving apart at speeds of 40, 30, 20, and 10 in. per minute, the normal speed being 20 in. per minute.

The Schopper machine used was the latest model with autographic Schob attachment. The standard ring test-piece (7-cm. diameter, cross-section approximately 3 mm. $\times$ 3.8 mm.) is placed in position over two pulleys which during test rotate by virtue of the drive imparted to the lower one. Thus, in addition to being stretched, the ring also rotates and a more uniform distribution of the load is assured. No direct readings of load and elongation are necessary, as the true stress-strain curve of the rubber is automatically traced out on a graph by means of the special Schob attachment. Thus all stress-strain data are obtained without any calculation. On this particular machine, the speeds of extension (*i. e.*, pulley separation) are 16, 8, and 4 inches per minute, the normal speed being 16 inches per minute. It has previously been mentioned that 20 inches per minute is the normal Bureau of Standards testing speed, but when the lengths of the test-pieces are taken into account (1 in. on Bureau of Standards machine, 7 cm. on Schopper machine) it will be seen that the real rate of extension of the rubber on the Bureau of Standards machine is several times greater than on the Schopper.

It is well known that dumb-bell test-pieces give higher results than rings, and the difference is often quoted as anything from 10 to 20 per cent, but results show that it would be very difficult and inaccurate to introduce any general conversion factor.

Experiments have been conducted to determine the effect of variation in speed of extension upon tensile strength results, and the results are indicated on the following graph (Fig. 1). These are stress-strain curves obtained on the Schopper machine at three different speeds, both with a typical tread and typical tube compound.

It will be seen that there is no appreciable difference shown between the three different speeds with either compound, although above the last two or three hundred per cent elongation, it is possible to obtain three distinct curves. The variation in breaking figures, however, is so small as to render it impossible to say whether increased speed of extension leads to an increase or decrease in tensile and in ultimate elongation. Exactly similar curves have been obtained with dumb-bells on the Bureau of Standards machine, so it is evident that within available limits the speed of extension has no appreciable effect upon tensile values. It is of interest to note, however, that a high speed test has recently been developed by van Rossem, which is based on the observation that a very high speed of extension leads to a decreased elongation.

The next series of graphs will indicate an important difference between the use of dumb-bell and ring test-pieces, due to the well-known phenomenon of calender

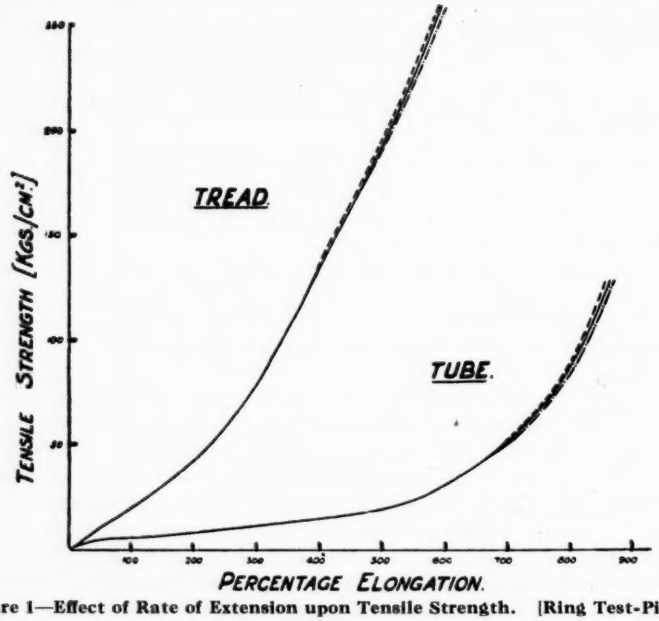

Figure 1—Effect of Rate of Extension upon Tensile Strength. [Ring Test-Pieces.]

grain. When preparing the test sheets for cure it is the custom to sheet out the rubber compound on a calender to the requisite thickness and to cure up in a mould. Such calendered sheet exhibits a greater strength, but smaller elongation in the direction of calendering than across this direction, and this phenomenon exists to some extent after cure. It is thus possible to obtain two different results on dumb-bells cut with and against the grain, while it is only possible to obtain the one result with ring test-pieces—that corresponding to break along the weakest direction. The next graph (Fig. 2), shows results obtained with both tread and tube compounds. Confining attention for a moment to the tube compound, the top curve is a stress-strain curve obtained from dumb-bells cut from along the direction of calendering, the middle one from dumb-bells cut against the direction of calendering, and the bottom one from ring test-pieces. All the test-pieces were cut from the same cured sheet, and each graph is the average of 20 determinations. The actual tensile

strength figures are: For the dumb-bells cut along the grain, 167 kg. per sq. cm., for dumb-bells cut against the grain, 147 kg. per sq. cm., and for rings, 128 kg. per sq. cm. This means a total variation of about 25 per cent. The figures on the tread give a different type of result and indicate how dependent the results are upon the method of preparation of test-piece. The breaking points are almost identical for all three types of the test-pieces, the actual tensile values for dumb-bells cut with and against the grain, and for rings, being 257, 255, and 258 kg. per sq. cm., respectively. This peculiar result has been traced to the fact that the test-pieces were cut from sheets which had been built up from thin calendered sheet, and toward the latter portion of the extension the dumb-bells showed a tendency to laminate, with a resulting lowering of tensile values. The actual fractures on the dumb-bells were jagged, while those on the rings were perfectly clean. If

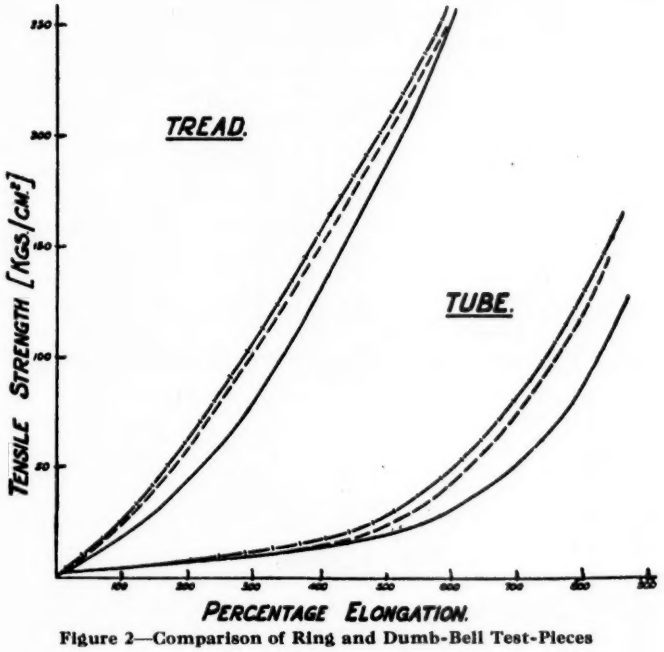

Figure 2—Comparison of Ring and Dumb-Bell Test-Pieces

adhesion between the different plies of a built-up test sheet is very bad, complete ply-separation may occur during extension, and the break, both with dumb-bells and rings, may occur in two distinct portions, although this tendency is always greater with dumb-bells. It is recommended that test-pieces wherever possible be cut from a single calendered sheet and that dumb-bells be cut always along the direction of calendering. A variation between rings and dumb-bell results may then be observed even up to 25 per cent, depending upon the amount of grain and the type of compound. Figure 3 shows the tensile values of different compounds, using the different test-pieces all cut from a single calendered sheet. It will be seen that the tread in this case gives a result quite different from that previously recorded on a built-up sheet.

Experiments have been carried out to investigate what actually determines the

breaking point of a ring test-piece. There are at least two factors which contribute to the lower figures which are generally obtained with rings. (1) The fact that the inside of the rings is stretched more than the outside, resulting in an uneven dis-

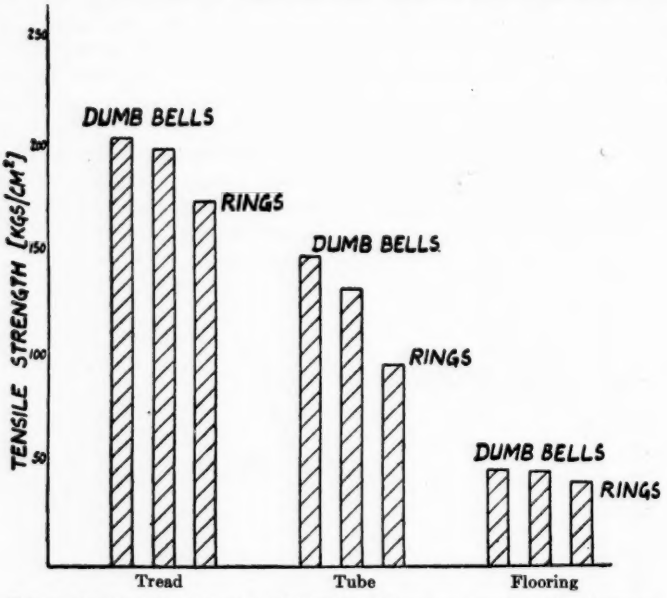

Figure 3—Tensile Strength of Typical Mixes on Scott and Schopper Machines

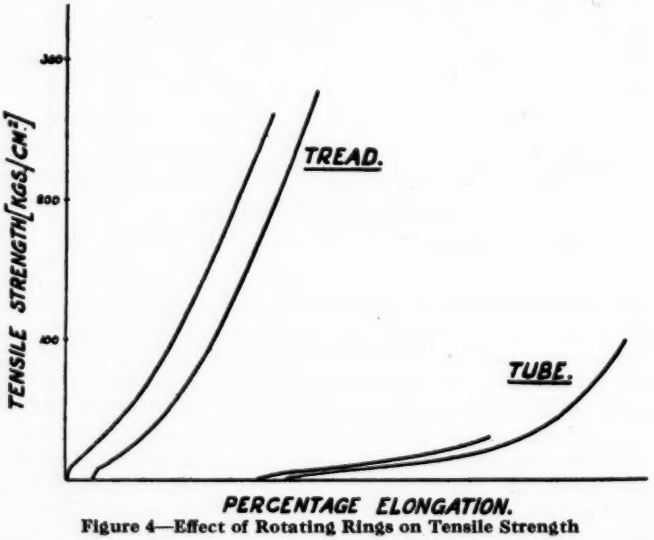

Figure 4—Effect of Rotating Rings on Tensile Strength

tribution of the load, and (2) in addition to being stretched under load, the ring is subjected to added distortion both on the upper and lower pulleys. By marking

the direction of calendering on a large number of rings, it can be proved that the test-piece almost invariably ruptures along this direction, and also that in the great majority of cases, rupture occurs at a point either on the top or bottom pulley. Thus, in general, it seems that the ring will break only when the direction of calendering coincides with the pulleys. This incidentally is a point in favor of using the average and not the minimum cross-section of test-piece for purposes of calculations. There has been much controversy on this point.

When ring test-pieces were first introduced it was the custom to stretch them over fixed pegs rather than over rotating pulleys, and breaking figures obtained in this way were very much lower. The next graph (Fig. 4), indicates the effect of rotating test-pieces upon the stress-strain curves of tread and tube mixes. In each case the fixed ring shows lower breaking figures than the rotating ring, particularly in the case of the tube compound, the reduction in tensile being about 50 per cent. This is due to the distortion which occurs at the point of contact between ring and pulley, and this, of course, is greater in the case of a tube than a tread compound. The tendency of all results is to indicate a greater difference in tensile values between ring and dumb-bell test-pieces for soft mixes than for hard ones.

It has previously been stated in the literature that any series of compounds will be placed in the same relative order of tensile strength values whether tested by the dumb-bell or ring method, but the results above show that only when strict precautions are taken to eliminate any undue strain in the test-piece, such as grain or lamination effects, does this assumption apply.

All tests mentioned in this paper were carried out at 18° C., and all figures quoted are the average of twenty test-pieces, both rings and dumb-bells.

In conclusion, the author wishes to express his thanks, for permission to publish these results, to the British Dyestuffs Corporation, Ltd., in whose laboratories, under the direction of W. J. S. Naunton, these experiments were carried out.

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A Simplification and Improvement in the Determination of Copper in Fabrics and Rubberized Materials

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The ordinary method used by many laboratories for the determination of small quantities of copper in fabrics and rubberized materials has in recent years been described in different journals.[1] This method consists essentially of ignition of the sample, repeated treatment of the ash with concentrated hydrochloric acid and potassium chlorate (Ruthing), or nitric acid and concentrated sulfuric acid (Kluckow and Siebner), precipitation of the copper as copper sulfide, solution of the latter, and colorimetric determination of the copper as the cuprammonium ion. Experience has shown that this method can be both simplified and improved.

The simplification is concerned especially with the ignition of the organic substances, which is a tedious operation, particularly in the case of rubberized materials, because the remains of the carbon are held tenaciously by the ash. Furthermore, in the case of rubber containing chlorine, there is danger that part of the copper will volatilize as chloride. This volatility of copper chloride is utilized in the detection of sulfur chloride factice in rubber products or, in the absence of factice, for evidence of cold vulcanization. In this case a glowing copper wire is brought in contact with the rubber, whereupon by subsequent introduction of the wire in a Bunsen flame the presence of chlorine is manifest by a blue-green flame.

The shortcomings of the older method can be overcome by cutting the sample into coarse pieces (10–20 grams), wetting with dilute nitric acid in a covered beaker, adding concentrated nitric acid (10–20 cc.), letting stand and completing the decomposition by heating on a water bath. After no more nitrogen tetroxide is evolved, which is about one hour, the nitro product is transferred by a glass rod to a large porcelain crucible, the residue on the rod is dissolved in a few cc. of acetone, and is rinsed into the crucible, with a few drops of concentrated ammonium hydroxide which is kept covered by a perforated watch glass, and is evaporated to dryness on a sand bath. A small flame is used to destroy the nitro compounds, and then a more intense flame to complete the ignition. The spongy carbonaceous residue, which is impregnated with ammonium nitrate, burns easily and actively, and the complete decomposition and ashing can be finished in $1^1/_2$ to 2 hours, whereas in the ordinary combustion and ignition, several hours are often required to remove all of the carbon from the ash. The reason for this is that the carbon from the fabric, and particularly that from the rubber, burns with much more difficulty than does the carbon of the nitro compounds; furthermore, in the nitric acid method, all of the soluble heavy metal oxides are present as nitrates and these, together with the ammonium nitrate, support the combustion.

The ash is digested with a few cc. of concentrated hydrochloric acid and a few cc. of dilute nitric acid on a water bath, the undissolved residue is removed by filtration, and the process is repeated after washing with hot water. The filtrate is made alkaline with a slight excess of concentrated ammonium hydroxide and is then brought to boiling. The precipitate, which consists chiefly of ammonium and iron

hydroxides, but occasionally also of other heavy metal hydroxides, is allowed to settle, is decanted through a small filter, and washed 2 or 3 times with a few cc. of hot water containing ammonia. Since the proportion of copper in the precipitate is a variable quantity, the precipitate is dissolved in a few drops of concentrated hydrochloric acid and again precipitated with a few cc. of dilute ammonium hydroxide. It is then filtered through the same filter, is treated as before, and the combined filtrates of the first and second precipitation are used (if necessary after preliminary concentration) for the calorimetric determination of the copper. After the second precipitation, the hydroxide precipitate contains around 1 to 2 per cent of the total copper present, which can in most cases be neglected. The following results are representative of the quantities of copper found in the hydroxide precipitate for different concentrations of copper.

I. Quantity of $FeCl_3$, 0.100 g.; quantity of $CuCl_2$, 0.017 g. (corresponding to 0.008 g. Cu) dissolved in 25 cc. of water. First precipitate, 0.00064 g. Cu, *i. e.*, 8 per cent of the total Cu; second precipitate, 0.00020 g. Cu, *i. e.*, 2.5 per cent of the total Cu.

II. Quantity of $FeCl_3$, 0.120 g. (corresponding to 0.08 g. $Fe(OH)_3$); quantity of ammoniacal Cu solution, 6 cc. (corresponding to 0.000846 g. Cu). First precipitate, 0.000030 g. Cu, *i. e.*, 3.5 per cent of the total Cu; second precipitate, 0.000010 g. Cu, *i. e.*, 1.2 per cent of the total Cu.

Ordinarily fabrics which are to be rubberized contain around 5 to 15 mg. of copper per square meter, and therefore a sample of about 5 square decimeters to be analyzed contains around 0.25–0.75 mg. of copper. An error of 1 to 2 per cent as a result of fixation of copper in the hydroxide precipitate corresponds to 0.0025 to 0.0075 mg. and 0.05 to 0.15 mg., respectively, of copper per square meter. These are errors which are within the required limits of accuracy. Furthermore, it must be borne in mind that the theoretically exact precipitation of copper as sulfide has the disadvantages, apart from the disagreeable use of hydrogen sulfide, of danger of losses resulting from the colloidal character of copper sulfide and the partial solubility of the latter through atmospheric oxidation. Numerous copper determinations carried out by the new method have given copper values which average several thousandths to one-hundredth per thousand higher than the values obtained by the two older methods cited.

The improvement in the determination of small quantities or even traces of copper in fabrics and in rubberized materials is a result of the application of the well-known and very precise iodometric determination of copper by colorimetry. The reaction involves the reduction of the cupric ion to the cuprous ion by hydrogen iodide with liberation of iodine, according to the reaction: $Cu^{++} + 2I^- \longrightarrow CuI + I$. The yellow cuprous iodide which separates at higher concentrations of copper does not add any complications to the reaction where such small quantities are concerned. With very dilute copper solutions, in which little or no blue color is visible with ammonia, the iodometric reaction still gives results which can be interpreted quantitatively, for the intensity of the color of the iodine corresponding to these traces of copper is about 10 times as intense as that of the complex cuprammonium coloration.

For this colorimetric reaction to be of practical value, ferric ions and nitric acid must be completely absent in the solution to be examined, for these substances likewise precipitate iodine from hydrogen iodide. Accordingly, the iron-free, ammoniacal solution, obtained by the procedure described, and in which copper could be determined only inaccurately, is acidified with a few drops of pure dilute sulfuric acid, concentrated on a water bath, and the sulfuric acid expelled by further cautious heating. This also volatilizes the hydrochloric acid and nitric acid.

The residue is dissolved in a few cc. of distilled water, and 1–2 cc. of 5 per cent potassium iodide solution and a few drops of dilute sulfuric acid are added. With traces of copper the solution acquires a distinct yellow color, and can be compared with standard solutions of known content prepared in the same way. It is convenient to use a solution containing 0.05 mg. of copper per cc. Solutions of 0.001 per cent copper still show a distinct yellow color. Their intensity can be increased tenfold by the addition of a few drops of starch solution. The colorimetric determination of the iodine solution is preferably made immediately after the color appears, for the solutions become darker upon standing as a result of the separation of iodine from oxidation of hydrogen iodide by atmospheric oxygen, and this leads to deceptive results.

It must be remembered that the investigations of Fleury and Garreau[2] show that in all colorimetric determinations, even when carried out under the most favorable conditions, there is an average error of about 1.5 per cent, which may in some cases reach 3 to 5 per cent. Therefore it is uncertain whether slight differences in the intensity of color of yellow solutions can, in general, be distinguished better than can blue solutions.[3] The physiological sensitivity of the individual for the different colors plays in this case the determinant part.

For the qualitative detection of traces of copper (*e. g.*, less than 0.02 mg. per cc.), the method proposed a few years ago by Spacu[4] can also be used. This method depends upon the appearance of an intense blue color or a flocculent cornflower blue colored precipitate on addition of a few cc. of benzidine in alcohol and a few drops of potassium iodide solution to neutral solutions containing traces of copper but free of other metals.

It may be added that preliminary experiments[5] indicate that this coloration and precipitate does not depend, as thought by Spacu, upon the formation of blue benzidine-copper iodide, but most probably upon the formation of a blue adsorption compound of iodine with benzidine or an oxidation product of the latter, like the iodine-starch product. Even small quantities of free iodine and all reactions in which free iodine is liberated, *e. g.*, the reduction of ferric to ferrous ion, give the blue coloration mentioned. This last view is supported by the fact that the intensity of the color depends upon the concentration of the iodine, as in the starch-iodine reaction.

Summary

The determination of small quantities of copper in fabrics and in rubberized materials can be simplified by destruction with concentrated nitric acid, which accelerates the ignition to the final ash. At the same time, this method avoids the usual danger of volatilization of copper as chloride as a result of the presence of chlorine from white factice or from cold vulcanization. Likewise, precipitation of the copper as sulfide can be avoided by repeating the precipitation of the extract from the ash, which contains predominantly aluminum and iron, with ammonia.

In this second precipitation, only around 1 to 2 per cent of the total quantity of copper is retained in the precipitate and filter, and this quantity may in most cases be neglected.

The ordinary colorimetric method used in the past for the detection of copper as complex cuprammonium ion can be made about ten times as sensitive by making use of the reaction: $Cu^{++} + 2I^- \longrightarrow CuI + I$. This is, however, applicable only in the complete absence of the ferric ion and of nitric acid in the test solution. The sensitivity can be increased still more by the addition of starch.

Another advantage of the determination of copper by measurement of the equivalent quantity of iodine lies in the fact that, if necessary, only one-tenth as

much sample need be used, but in this case as in all such determinations, the copper must be distributed uniformly throughout the material to be analyzed.

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[2] *Chem. Zentr.*, **1924**, II, 728.
[3] *Chem.-Ztg.*, **1926**, 898.
[4] *Z. anal. Chem.*, **67**, 31 (1925–6).
[5] Further details are to be reported elsewhere.

[From Transactions of the Institution of the Rubber Industry, Vol. 7, No. 1, pages 81–84, June, 1931.]

The Determination of Free Sulfur in Soft Vulcanized Rubber by a Volumetric Method

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The methods so far proposed for the determination of the free sulfur in vulcanized rubber depend upon the removal of the sulfur by extraction of the rubber with hot acetone, and subsequent oxidation to sulfuric acid of the sulfur in the extract. The extract is liable however to contain, in addition to sulfur in the elementary state, organic compounds containing sulfur derived from the rubber

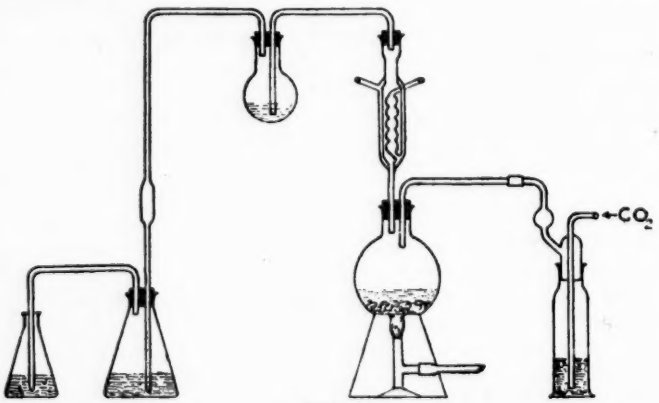

Figure 1

resins, accelerator, or antioxidant. In the subsequent oxidation this sulfur will be oxidized to sulfuric acid to an extent which depends on the method of oxidation used.

In the present work, a method of analysis has been developed which is more rapid than the existing methods, and in which it is considered that the determination of the sulfur present in the elementary state is less likely to be affected by organic compounds containing sulfur.

It has been found that when vulcanized rubber placed in contact with a metal, such as tin or aluminum, is boiled in hydrochloric acid, hydrogen sulfide is generated by the action of the nascent hydrogen produced. This reaction occurred with rubber which had been previously treated with acid alone to decompose metallic sulfides, but no hydrogen sulfide was obtained from rubber which had been previously extracted with acetone and was free from metallic sulfides. As these results showed that the reactions were not due to the presence of mineral sulfides, or of sulfur combined with the rubber, it was concluded that the hydrogen sulfide was formed by the reduction of the free sulfur.

By a suitable modification of the conditions, it has been found possible to obtain quantitative reduction of the sulfur in 1 to $1^1/_2$ hours.

Experimental Details

To obtain a uniform and finely divided sample, the rubber was passed between rollers running at different speeds. Two grams of the rubber cut into small pieces were weighed out into a beaker and boiled with concentrated hydrochloric acid for 1 to 3 hours to decompose any mineral sulfides. In the case of rubbers containing antimony sulfide, the full three hours' boiling was given. The acid was removed by decantation, the rubber was washed two or three times either by filtration or decantation, and was transferred to a 600-cc. wide-necked flask containing about 50 grams of granulated tin (see Fig. 1).

The flask was closed with a specially prepared rubber stopper free from sulfides, and was fitted with a reflux condenser and an inlet tube from a source of carbon dioxide gas. The carbon dioxide was freed from hydrogen sulfide by passing it through a wash-bottle containing a solution of lead acetate and acetic acid. The hydrogen sulfide evolved was carried by a stream of carbon dioxide through the reflux condenser and through a flask containing distilled water, where the last traces of acid were removed, and then into two absorption flasks in series, each filled to a depth of 2 cm. with a solution of cadmium acetate (25 g. cadmium acetate, 100 cc. glacial acetic acid per liter).

100 cc. of a mixture of equal volumes of glacial acetic acid and concentrated hydrochloric acid were added to the metal and rubber in the reaction flask, a steady stream of carbon dioxide was passed through the apparatus, and the acid mixture was boiled vigorously for $1^1/_2$ hours.

The apparatus was then disconnected, and any cadmium sulfide formed in the second absorption flask was transferred to the first. In experiments using the above apparatus the amount of sulfide formed in the second flask did not exceed a trace, and a third flask was found to be unnecessary. Excess of standard decinormal iodine solution was run in and 5 cc. of concentrated hydrochloric acid were added. After allowing the solution to stand for a few minutes, the excess iodine was titrated with decinormal sodium thiosulfate solution. The amount of free sulfur in the sample was calculated from the volume of iodine solution used in the oxidation of the sulfide.

The results obtained by this method were compared with results obtained by the oxidation of the acetone extract by the following methods.

The first method is that of Tuttle, and is adopted as standard by the Rubber Division of the American Chemical Society.

This consists in treating the acetone extract with 2–3 cc. bromine and 100 cc. water, heating gently on a water bath for $^1/_2$ hour, and then more strongly to expel the excess bromine. The resins, which are not destroyed by this method, are filtered off and barium chloride is added to the filtrate in the usual way.

In the second method (Caspari, "India Rubber Laboratory Practice"), the sulfur and resin are completely oxidized with 30–40 cc. of concentrated nitric acid and 2 g. of potassium chlorate, the solution is taken to dryness on the water bath, 20 cc. of concentrated hydrochloric acid are added, and the solution is evaporated to dryness again. After the addition of 2–3 cc. of concentrated hydrochloric acid, the solution is diluted to 400 cc., and barium chloride is added in the usual way.

Some results obtained by the methods above are given in Table I.

Except in the case of sample 5, good agreement is obtained between the direct reduction method and the method due to Tuttle. In some cases the latter method gives a result lower than that obtained by the complete oxidation of the acetone extract with nitric acid and potassium chlorate, and it is considered that this is due to the incomplete oxidation by bromine of the sulfur combined with organic

TABLE I

Composition of Vulcanized Mixing	Free Sulfur by Reduction with Tin + Hydrochloric Acid, %	Free Sulfur by Oxidation of Acetone Extract (1) with Bromine + Water, %	Free Sulfur by Oxidation of Acetone Extract (2) with Nitric Acid + Potassium Chlorate, %
1. Rubber 100 parts Sulfur 10 parts	5.61 5.60 5.56	5.58	5.74
2. Rubber 100 parts Zinc oxide 112 parts Sulfur 4 parts Diphenylguanidine 1 part	0.55 0.56	0.53	
3. Rubber 53 parts Zinc oxide 13.5 parts Carbon black 31 parts Sulfur 2.5 parts	0.19 0.20	0.21	0.25
4. Rubber 80 parts China clay 10 parts Antimony sulfide 8 parts Sulfur 1.8 parts	1.38		1.35
5. Rubber 87 parts Zinc oxide 10 parts Sulfur 2.5 parts Vulcafor resin 0.5 part	0.83 0.87	1.00	1.14

compounds. In the case of sample 5, the difference in the results given by the two methods of oxidation of the acetone extract indicates the presence of organic compounds containing sulfur. This sulfur is probably partly oxidized to sulfuric acid by bromine, and in consequence the method due to Tuttle gives a result higher than that obtained by the direct reduction method.

The author desires to thank T. J. Drakeley for his interest and help in the work.

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An Investigation of the Causes of Spots Which Appeared Spontaneously on Rubberized Fabrics

G. Martin in Collaboration with J. Sisley

The opportunity was offered to examine a white rubberized fabric on which rose-colored spots had developed spontaneously. This fabric was to be used in the manufacture of white footwear, and was constructed of two plies of fabric, a white cloth and an unbleached cretonne cemented together by a rubber solution.

On certain pieces of the plied fabric and on certain lots of the finished footwear, there gradually appeared patches of a rose color, which were especially prevalent on the unbleached fabric and on the white edge of the footwear.

Since both unblemished cloth and cloth in various stages of spotting were available for examination, an investigation was made of the differences between the good and the bad fabrics, and of the causes of the rose-colored spots.

An unbleached sample of cloth on which the rose-colored blemishes were intense was first examined. In this case extraction with boiling water gave a liquid with a slight acid reaction.

Another portion of the same cloth, treated with 20 per cent acetic acid, yielded a dye, the reactions of which indicated that it belonged to the triphenylmethane group of dyes, since it resembled fuchsin and rosaniline. The presence of an aromatic amine in the aqueous extract could not be established.

On the other hand, when a piece of the unbleached cloth which showed only the first signs of alteration was extracted with water, a slightly acid solution was obtained which absorbed nitrous acid and then could be coupled with β-naphthol. This indicated the presence of a primary aromatic amine in the aqueous product.

To prove this in a still clearer way, a part of the aqueous extract was concentrated and was treated with diazo-*p*-nitroaniline solution in the presence of sodium acetate. An orange coloration immediately appeared, and at the end of one-quarter hour an orange precipitate formed. This precipitate was filtered, washed, and dissolved in pyridine. The pyridine solution diluted with water dyed a skein of cellulose acetate a yellow color. The yellow dye fixed on the fiber was in turn diazotized and coupled with β-hydroxynaphthoic acid, which gave a reddish tint characteristic of an aminoazo derivative of *p*-nitroaniline. In a control test, diazo-*p*-nitroaniline gave no such coloration.

This reaction showed therefore the presence in the rubberized fabric of an aromatic amine. The same series of tests, carried out on the aqueous extract of the finely divided rubber, gave similar results.

On the other hand, with fabrics which had been manufactured longer than the other samples, but which nevertheless showed no rose-colored spots, the color reactions described above were not observed. Moreover, the aqueous extract contained a small quantity of soap, and had a slightly alkaline reaction.

These tests led therefore to the conclusion that the rose-colored spots were only a manifestation of the well-known oxidation of aromatic bases in an acid medium in the presence of air. This phenomenon was moreover easily reproduced at will.

When a fabric was soaked in a saturated aqueous solution of aniline, eventually there appeared only a very faint beige-rose coloration, which was probably the result of the acidic atmosphere in the laboratory. On the other hand, when the fabric was moistened with a solution of aniline hydrochloride (of the corresponding concentration) the rose coloration was very pronounced.

Moreover, fabrics coated with rubber solutions containing in one case traces of aniline and in the other traces of an aniline salt were prepared. Only in the second case did rose-colored spots appear.

These artificial tests accordingly confirm the conclusion already drawn. It remained to determine the origin of the factors responsible. Since the rubber gave the color reaction very distinctly, it was probably the source of the amine, which was present as a plasticizing agent or as an accelerator. As for the acid, it may be assumed that it came from the sizing of the fabric. It is not, however, safe to be too certain of this, for it was found that the rubber on spotted fabrics had deteriorated and had lost its adhesive properties, probably as a result of the effect of traces of copper which were detected in the fabrics. Does the transformation of rubber catalyzed by copper salts give acid products? A knowledge of this would be one step nearer to an answer to the problem just discussed.

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Lipin from Latex

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Recent papers by Rhodes and Bishop[1] and by Eaton, Rhodes, and Bishop[2] have described work carried out at the Rubber Research Institute of Malaya on the isolation of lipin from the serum of latex, and its effect on vulcanization. Aside from its accelerating power, it was found that when it was added to rubber during mastication on hot rolls, the plastic mass became opaque and had a great tendency to crumble.

The receipt of about four ounces of lipin extracted from *Hevea* latex gave the opportunity to verify this peculiar effect of lipin on rubber during mastication and to find some industrial application of this property.

Approximately two hundred grams of pale crepe rubber were masticated on a small experimental mill until the rubber ran around the front roll in a smooth sheet. Two grams of the waxy lipin were then added. This did not adhere to the rubber, but rolled around in a lump on the bank of rubber at the nip. As the surface of the masticating rubber became smeared with the lipin, the sheet coming around the front roll began to break up, as if it were scorching, and in a few moments the rubber began to crumble like vulcanized scrap being shredded. After a time, the lipin worked into the rubber, which then reunited in the form of a sheet.

When the mixing was finished, it had a slightly greasy feeling, and did not have the same amount of self-adhesion that pure gum usually does. The explanation of the behavior of lipin during mastication seems to be found in the fact that, although such an excellent lubricant, it has not the slightest solvent action upon rubber. A slightly similar behavior during mastication can be reproduced by adding glycerin to the rubber, although in this case the crumbling is not nearly so marked.

A number of further experiments showed that the lipin from latex has an extraordinary power to prevent self-adhesion of masticated rubber. By means of an atomizer, freshly calendered hot pure gum stock was sprayed with a minute quantity of two per cent of lipin-in-ether mist, and in this way it was proved that the treated sheet will not stick when folded, even when left in contact for a long time.

Though not suggesting that *Hevea* lipin can be used industrially for such a purpose, it does seem possible that other available substances of similar constitution and properties, such as egg lecithin, may find application in replacing dusting powders and cloth liners. The advantages of replacing such powders as talc and zinc stearate with a trace of lecithin, which is quite dustless, can be imagined. Preliminary tests suggest that wiping the surface with a rag moistened with solvent, renews the adhesive character; furthermore, the lipin seems to disperse during curing, so that ply-separation is unlikely in articles built up from such treated calendered sheet. The lecithin might be sprayed or brushed on as a dilute water-emulsion, or it might be introduced by running the calendered sheet or frictioned material over a treated roller, after which the sheet could be rolled up without a liner.

Egg lecithin is now commercially available because it is already used in the chocolate industry, and lipins obtained from the soy bean are now available, so further experiments on this same subject are contemplated.

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[2] Eaton, Rhodes, and Bishop, Rubber Research Inst. Malaya, *Quart. J.*, **2**, 136–138 (1930); RUBBER CHEMISTRY & TECHNOLOGY, **4**, 339–344 (1931).

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Studies in the Vulcanization of Rubber

V. Dielectric Constant and Power Factor of Vulcanized Rubber

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This paper deals with two important dielectric properties of vulcanized rubber—dielectric constant and power factor. Data are given for samples containing from 2 to 32 per cent sulfur tested at 30°, 50°, 75°, and 100° C. at frequencies from 600 to 2,000,000 cycles. These electrical properties vary greatly with composition, frequency, and temperature. The dielectric behavior has been interpreted in previous papers (2, 8) on the basis of polar molecules. In this paper it is shown that this theory, as originally applied to rubber, requires some modification. The results do not disprove a dipole mechanism, but they do show that the low dielectric constant and power factor of hard rubber at room temperature, which led to the belief that addition of sulfur to all the double bonds gave a balanced molecule, are really due to its rigidity, which so retards the electrical response that the period of charge or discharge is 24 hours or more. At higher temperatures hard rubber softens, the period becomes short, and dielectric constant and power factor are high.

Studies of the compressibility and thermal expansion of vulcanized rubber have revealed two states with

a fairly sharp transition temperature: a hard state in which rubber resembles a solid, and a soft state in which it exhibits properties of a viscous liquid. The dielectric behavior also is greatly influenced by this transition and in a manner which gives additional support to the concept of soft rubber as a liquid.

It is shown that the agents producing the electrical effects are not identical, but possess widely different relaxation times. Preliminary tests show that the power factor of a vulcanized rubber sheet decreases on stretch. None of the data makes it possible to determine the actual mechanism of the electrical behavior.

THE peculiar dielectric behavior of vulcanized rubber discovered by Curtis, McPherson, and Scott (*3*) was attributed by them to definite rubber-sulfur compounds. Their curves of dielectric constant and power factor at 1000 cycles *vs.* per cent combined sulfur showed maxima at definite stoichiometric proportions. It was shown later by the writer (*8*) that these maxima could be continuously shifted to other rubber-sulfur proportions by changing the test frequency. Change in temperature has a similar effect. Thus the electrical behavior cannot be attributed to any particular definite compounds.

A different interpretation suggested by Boggs, and based on the hypothesis that addition of sulfur to rubber gives rise to dipolar molecules has been given in several papers (*2*, *8*). On this theory, progressive addition of sulfur to the double bonds of the rubber molecule made it more and more dipolar until approximately half of the double bonds were saturated. Further addition by restoring the balance again gave a compensated nondipolar molecule.

This compensation idea was supported chiefly by the curve of d. c. dielectric constant *vs.* per cent sulfur at room temperature (*8*) in which the dielectric constant, after rising almost linearly with added sulfur to about 4.9 at 14 per cent sulfur drops to below 3.0 beyond 19 per cent sulfur. These low values correspond to a mere mixture of rubber and sulfur, and it was therefore argued that the rubber-sulfur molecules must be electrically balanced, because otherwise they should show some effect on a static or direct current test. The low power factor of hard rubber over a wide frequency range at room temperature and its general excellence as a dielectric also led to the same conclusion.

It was shown, however, by unpublished results of Curtis and Scott, and by tests in this laboratory that the power factor and dielectric constant of hard rubber increase with tempera-

ture, and that the maximum in the dielectric constant in the intermediate sulfur region disappears. Indeed at 100° C. the low-frequency dielectric constant increases continuously up to the highest sulfur percentage. Unless the unlikely assumption was to be made that molecules electrically balanced at room temperature broke down into dipolar ones at higher temperature, it was necessary to conclude that the agents responsible for the effect at higher temperature, whether dipoles or something else, are present also at low temperature, but are prevented from responding by the rigidity of the material.

The errors in interpretation stated above were thus due in the one case to tests made only at a single frequency, and in the other, at only one temperature. It was desirable, therefore, from these and other considerations to carry out tests over a wide frequency range and at several temperatures in the attempt to determine the mechanism involved in the

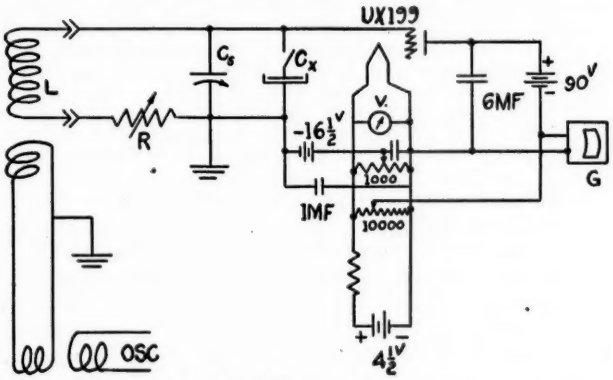

FIGURE 1. MEASURING CIRCUIT

electrical behavior. The work described in this paper was undertaken to that end.

While the results do not enable us to decide what the real mechanism is, they show some interesting aspects which are believed to warrant their publication.

APPARATUS AND METHODS

The audio frequency tests were made by means of a General Radio, Type 216 capacity bridge with no novel features. A shielded two-stage audio amplifier was inserted between bridge and ear phones to increase the sensitivity. The audio frequency waves were picked up by a coil loosely coupled to the oscillator, amplified through two stages, and passed to the bridge through a shielded cable.

The same oscillator was used for both audio and radio frequencies, the wide range from 600 to 2,000,000 cycles being covered by the use of a series of plug-in coils and various capacity combinations. For the audio frequency waves, it

was adjusted to zero beat with the output of an induction generator driven by a synchronous motor. For radio frequency settings, a General Radio precision wavemeter was used.

The radio-frequency measuring circuit is shown in Figure 1.

The measuring apparatus was placed about 20 feet (6 meters) from the oscillator on a table with a grounded metal top. Coil L was coupled to the oscillator by a grounded, untuned coupling link. At the measuring table the line was shielded for 6 feet (1.8 meters) by a grounded brass tube.

L represents the tuning inductance. In order to cover conveniently the radio frequency range from 13 to 2000 kilocycles with C_s (a 1500 mmf. General Radio precision condenser), a set of plug-in coils was used. R is a General Radio decade resistance box with noninductive units in 0.1-ohm steps. C_x represents the sample under test. At the right of C_x is shown the vacuum tube voltmeter used to indicate resonance and measure the response. A plate voltage of 90 volts was used and a negative grid bias of -16.5 volts to keep the radio peak voltage from exceeding the bias, a condition which would cause grid current to flow and introduce damping into the resonant circuit. The grid return was connected to a potentiometer to permit the most sensitive operation of the tube. The residual steady plate current was balanced out by means of the 10,000-ohm potentiometer. G is a Weston four-range milliammeter, which can be read to a fraction of a microampere. The high sensitivity of this meter made possible very loose coupling to the oscillator, which was thus independent of changes in the measuring circuit.

The measurements were made as follows: With C_x connected, C_s was tuned to resonance at say C_1, giving response G_1. C_x was then disconnected and C_s retuned to resonance at C_2. G was kept on scale without added resistance R by setting G on a lower range if necessary. Then $C_x = C_2 - C_1$. Resistance R was then added while C_s was carefully tuned, until G was brought back exactly to G_1. R was the value of resistance which produced the same damping in the circuit as the losses in C_x. Then the equivalent series resistance of the sample,

$$R_x = R\left(\frac{C_2}{C_x}\right)^2 \tag{1}$$

and the power factor,

$$PF = \omega C_x R_x \tag{2}$$

where $\omega = 2\pi_x$ frequency

The preliminary power factor *vs.* frequency curves were very irregular in spite of careful measurement, whereas the corresponding capacity curves were smooth. Duplicate samples checked closely. The trouble, therefore, was not due to freak samples, nor did such erratic behavior seem characteristic of rubber in general. Tests showed a similar effect with castor oil of known properties; so that the trouble was due to method rather than to sample.

The hidden error was finally found to lie in the use for C_2 in Equation 1 of the calibration value of C_s. Besides the shunt

capacity of the vacuum tube voltmeter, there is the capacity of the circuit to ground, the input capacity of the vacuum tube, and the distributed capacity of the coils. The effective additional shunt capacity of the circuit was therefore determined for each coil, and found to vary in an irregular manner from about 10 mmf. with the smallest coil to 37 mmf. with the largest. It may be seen from Equation 1 that neglect to correct for this additional shunt capacity can cause a large error in R_s and in power factor without affecting the accuracy of the values for C_s and the dielectric constant, which depend only on the difference, $C_2 - C_1$. When the corrected values for C_2 were applied, the data fell on smooth curves.

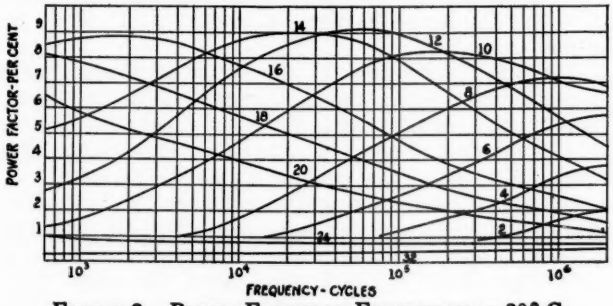

FIGURE 2. POWER FACTOR *vs.* FREQUENCY AT 30° C.

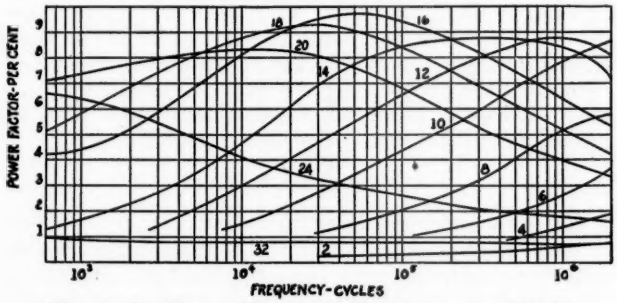

FIGURE 3. POWER FACTOR *vs.* FREQUENCY AT 50° C.

The samples were made from washed, dried, smoked sheets, and sulfur without accelerator. They were cured 6 hours at 300° F. (148.9° C.). The free and combined sulfur were determined by a standard method. The results are shown in Table I.

TABLE I. DETERMINATION OF FREE AND COMBINED SULFUR

SAMPLE	COMBINED S	FREE S	SAMPLE	COMBINED S	FREE S
	%	%		%	%
2	1.96	0.08	14	13.00	1.36
4	3.80	0.30	16	15.03	0.81
6	5.00	0.43	18	16.96	0.71
8	6.96	0.63	20	19.36	0.69
10	8.22	1.27	24	22.57	0.60
12	9.79	1.13	32	28.41	3.33

Sample thicknesses were the averages of measurements with a Randall-Stickney gage at five points on the tested areas.

Several types of electrodes were tried on the rubber sheets but gave poor contact. Molded-in disks were not used because it was desirable to vacuum-dry the sheets. The method finally used was to apply a very thin coat of dilute rubber-benzene solution to disks of metal foil, which were rolled into intimate contact with the rubber after evaporation of solvent. For test, the samples were placed between silver-plated disks of 0.25-inch brass of the same diameter as the foil electrodes. These gave good conductance over-all and minimized temperature fluctuation.

The samples were tested in air bath kept constant within 0.2° C. at the lowest temperature and about 1° C. at the highest.

Since it had been reported by Scott that there was a lag in the electrical properties when rubber was heated, the samples were brought slowly to temperature, and, after an hour or more at the desired temperature, preliminary measurements were made to ensure that equilibrium had been reached.

Such a lag in electrical properties would be very interesting theoretically; tests were therefore made to detect it. Samples of different sulfur contents were rapidly heated from room temperature to 100° C., and power factor tests made simultaneously. The reverse process was also carried out. The samples were rapidly cooled from 100° C. in cold water, wiped dry, and tested immediately. Such tests at several frequencies failed to show any detectable lag. The power factor always corresponded to the new temperature. Scott later stated that the apparent lag was due to experimental conditions. However, in all the measurements ample time was allowed for establishment of temperature equilibrium.

Experimental Results

The power factor and dielectric constant data at the various frequencies are given in Table II. The power factors are also plotted *vs.* log frequency. Dielectric constant data are not plotted because the curves would lie so close together as to be confusing. The variation with temperature and frequency for each composition can readily be seen from Table II. The numbers on the curves are the sample numbers as are given in Table I, not the sulfur contents.

General Discussion

The data show that, in general, the dielectric constant for a given composition falls with increase in frequency. Such a drop is usually accompanied by a corresponding power factor or loss maximum. This phenomenon, called "anomalous dispersion and absorption," is especially pronounced in the intermediate sulfur range at room temperature and in the high sulfur range above 50° C. Below 2 per cent sulfur it is practically negligible.

TABLE II. POWER FACTOR AND DIELECTRIC CONSTANT DATA

FREQUENCY	30° C.		50° C.		75° C.		100° C.	
	P. F.[a]	D. C.[b]	P. F.	D. C.	P. F.	D. C.	P. F.	D. C.
Kilocycles	%		%		%		%	
SAMPLE 2, 1.955% COMBINED S								
0.600	0.272	2.82	0.370	2.79	0.612	2.73	1.03	2.68
0.960	...	..	0.397	2.79	0.523	2.74	0.930	2.67
2.160	0.353	2.78	0.296	2.79	0.477	2.73	0.734	2.68
13.5	0.147	2.82	0.290	2.77	0.399	2.70	0.570	2.68
30	0.298	2.84	0.296	2.83	0.346	2.73	0.557	2.71
60	0.412	2.82	0.321	2.76	0.338	2.70	0.470	2.66
100	0.488	2.83	0.356	2.76	0.355	2.74	0.687	2.66
300	0.870	2.84	0.440	2.78	0.370	2.71	0.389	2.64
600	1.20	2.82	0.516	2.78	0.369	2.73	0.378	2.66
1000	1.71	2.78	0.650	2.74	0.450	2.70	0.352	2.61
2000	2.03	2.78	0.849	2.76	0.518	2.70	0.238	2.63
SAMPLE 4, 3.795% COMBINED S								
0.600	0.213	3.02	0.273	2.95	0.386	2.85	0.872	2.78
0.960	0.246	3.02	0.278	2.95	0.408	2.84	0.780	2.78
2.160	...	..	0.238	2.93	0.466	2.80	0.681	2.77
13.5	0.328	3.01	0.237	2.92	0.280	2.85	0.423	2.77
30	0.613	3.02	0.346	2.93	0.390	2.86	0.426	2.78
60	0.928	3.00	0.434	2.90	0.340	2.83	0.399	2.77
100	1.24	2.98	0.534	2.92	0.381	2.85	0.361	2.77
300	2.02	3.00	0.769	2.92	0.460	2.83	0.364	2.78
600	2.69	2.96	1.10	2.92	0.535	2.85	0.424	2.78
1000	3.41	2.90	1.44	2.86	0.725	2.80	0.560	2.72
2000	3.76	2.86	1.94	2.86	0.992	2.80	0.581	2.76
SAMPLE 6, 5.00% COMBINED S								
0.600	0.274	3.34	0.272	3.22	0.414	3.10	0.875	3.02
0.960	0.328	3.32	0.264	3.22	0.402	3.10	0.787	3.02
2.160	0.416	3.32	0.193	3.22	0.342	3.12	0.607	3.00
13.5	1.02	3.33	0.357	3.17	0.301	3.09	0.507	2.99
30	1.48	3.32	0.622	3.28	0.396	3.12	0.447	3.00
60	2.12	3.25	0.794	3.17	0.426	3.06	0.450	3.00
100	2.60	3.23	0.972	3.17	0.523	3.09	0.432	3.00
300	3.90	3.20	1.57	3.17	0.710	3.09	0.475	3.00
600	4.83	3.14	2.15	3.16	1.01	3.09	0.604	3.02
1000	5.44	3.05	2.82	3.10	1.30	3.04	0.699	2.97
2000	5.77	2.97	3.73	3.09	1.62	3.06	0.703	2.99
SAMPLE 8, 6.959% COMBINED S								
0.600	0.433	3.41	0.185	3.31	0.258	3.18	0.565	3.04
0.960	0.499	3.41	0.224	3.31	0.260	3.18	0.495	3.04
2.160	0.774	3.39	0.284	3.31	0.256	3.18	0.387	3.04
13.5	2.05	3.35	0.749	3.26	0.320	3.16	0.296	3.03
30	3.24	3.33	1.15	3.30	0.453	3.16	0.415	3.06
60	4.28	3.23	1.60	3.24	0.602	3.13	0.508	3.02
100	5.01	3.20	2.03	3.21	0.714	3.14	0.549	3.04
300	6.51	3.08	3.24	3.19	1.21	3.14	0.861	3.04
600	7.03	2.98	4.21	3.14	1.78	3.14	0.948	3.03
1000	7.13	2.88	5.17	3.08	2.37	3.09	1.74	3.00
2000	6.87	2.80	5.82	3.01	3.15	3.08	2.11	2.98
SAMPLE 10, 8.22% COMBINED S								
0.600	1.35	3.80	0.483	3.68	0.352	3.55	0.727	3.39
0.960	1.71	3.78	0.556	3.68	0.354	3.55	0.639	3.39
2.160	2.48	3.78	0.716	3.66	0.382	3.56	0.496	3.39
13.5	5.19	3.57	1.83	3.63	0.713	3.52	0.459	3.42
30	6.64	3.58	2.73	3.63	1.03	3.55	0.564	3.42
60	7.56	3.36	3.66	3.55	1.39	3.50	0.693	3.42
100	8.08	3.26	4.34	3.50	1.74	3.50	0.789	3.40
300	8.12	3.10	5.89	3.40	2.72	3.46	1.23	3.41
600	7.55	3.00	7.16	3.32	3.58	3.47	1.76	3.40
1000	7.09	2.90	7.79	3.18	4.47	3.31	2.32	3.33
2000	6.65	2.88	8.69	3.11	5.13	3.31	3.47	3.34
SAMPLE 12, 9.79% COMBINED S								
0.600	2.75	3.96	0.677	3.87	0.447	3.73	0.783	3.52
0.960	3.28	3.92	0.831	3.87	0.183	3.73	0.682	3.52
2.160	4.37	3.84	1.15	3.85	0.518	3.71	0.534	3.50
13.5	7.34	3.54	3.47	3.74	0.995	3.66	0.553	3.50
30	8.84	3.48	4.66	3.76	1.55	3.70	0.696	3.54
60	9.10	3.25	5.73	3.62	2.13	3.62	0.926	3.52
100	8.88	3.18	6.68	3.54	2.67	3.62	1.12	3.52
300	7.46	3.02	7.82	3.39	4.03	3.55	1.86	3.50
600	6.49	2.92	8.43	3.27	5.35	3.48	2.59	3.48
1000	5.70	2.82	8.81	3.11	6.31	3.40	3.27	3.41
2000	4.47	2.81	8.13	3.02	7.14	3.30	4.46	3.39

[a] Power factor. [b] Dielectric constant.

TABLE II. POWER FACTOR AND DIELECTRIC CONSTANT DATA
(*Continued*)

FREQUENCY	30° C.		50° C.		75° C.		100° C.	
	P. F.[a]	D. C.[b]	P. F.	D. C.	P. F.	D. C.	P. F.	D. C
Kilocycles	%		%		%		%	
	SAMPLE 14, 12.99% COMBINED S							
0.600	5.14	4.06	1.28	4.09	0.498	3.99	1.08	3.76
0.960	5.76	4.00	1.69	4.07	0.568	3.95	0.965	3.76
2.160	6.63	3.83	2.34	4.06	0.737	3.95	0.588	3.74
13.5	8.87	3.48	5.25	3.91	1.74	3.88	0.729	3.74
30	8.98	3.34	7.07	3.79	2.65	4.00	0.951	3.74
60	8.55	3.20	7.87	3.66	3.48	3.80	1.31	3.72
100	7.91	3.14	8.45	3.57	4.32	3.76	1.72	3.70
300	5.93	3.00	8.74	3.34	5.91	3.67	2.70	3.68
600	4.79	2.93	8.73	3.19	7.10	3.58	3.78	3.65
1000	4.15	2.86	8.51	3.08	8.10	3.42	4.74	3.57
2000	3.26	2.86	7.14	3.02	7.81	3.33	6.16	3.50
	SAMPLE 16, 15.03% COMBINED S							
0.600	8.54	3.81	4.17	4.38	1.13	4.37	1.01	4.14
0.960	8.71	3.72	4.56	4.33	1.32	4.34	0.941	4.12
2.160	8.84	3.53	5.28	4.23	1.70	4.32	0.827	4.11
13.5	7.47	3.22	8.59	3.84	4.00	4.18	1.43	4.09
30	6.64	3.20	9.51	3.74	5.44	4.14	1.99	4.09
60	5.58	3.03	9.66	3.54	6.57	3.97	2.76	4.00
100	4.78	3.00	9.39	3.41	7.42	3.92	3.44	4.01
300	3.44	2.94	8.02	3.21	8.78	3.67	5.21	3.93
600	2.93	2.91	7.15	3.14	9.48	3.56	6.86	3.78
1000	2.60	2.88	6.60	3.03	9.79	3.38	8.04	3.70
2000	2.06	2.82	5.29	2.97	8.59	3.27	9.62	3.58
	SAMPLE 18, 16.96% COMBINED S							
0.600	8.17	3.52	5.17	4.27	1.45	4.33	0.876	4.08
0.960	7.82	3.44	5.95	4.21	1.75	4.31	0.857	4.08
2.160	7.01	3.27	6.88	4.04	2.36	4.28	0.854	4.06
13.5	5.42	3.03	8.99	3.59	5.28	4.08	1.88	4.09
30	4.71	3.04	9.31	3.47	6.76	3.98	2.73	4.10
60	3.89	2.96	8.89	3.32	7.96	3.86	3.68	3.96
100	3.50	2.90	8.40	3.40	8.70	3.74	4.48	3.95
300	2.49	2.87	6.86	3.06	9.14	3.52	6.32	3.80
600	2.12	2.86	5.82	3.01	9.22	3.38	8.33	3.70
1000	1.95	2.80	5.29	2.92	9.22	3.23	9.74	3.54
2000	1.59	2.78	4.22	2.90	7.75	3.14	10.91	3.34
	SAMPLE 20, 19.36% COMBINED S							
0.600	6.51	3.43	7.16	4.25	2.33	4.61	0.951	4.41
0.960	5.98	3.36	7.43	4.19	2.84	4.60	1.02	4.39
2.160	5.13	3.27	7.58	4.01	3.65	4.52	1.26	4.39
13.5	3.67	3.06	8.26	3.58	6.76	4.23	3.08	4.39
30	3.17	3.11	8.06	3.47	8.13	4.10	4.08	4.34
60	2.69	3.02	7.44	3.34	8.97	3.92	5.32	4.23
100	2.38	3.00	6.82	3.27	9.26	3.80	6.26	4.16
300	1.86	3.00	5.22	3.16	9.10	3.59	8.32	3.96
600	1.66	2.98	4.48	3.10	8.86	3.45	9.97	3.81
1000	1.60	2.91	4.11	3.03	8.51	3.32	10.82	3.61
2000	1.19	2.96	3.37	3.02	6.83	3.23	11.12	3.46
	SAMPLE 24, 22.57% COMBINED S							
0.600	1.03	2.91	6.64	3.36	6.77	4.45	1.77	4.56
0.960	1.00	2.90	6.31	3.34	7.38	4.38	2.16	4.54
2.160	0.825	2.88	5.92	3.30	7.89	4.19	2.94	4.49
13.5	0.809	2.85	3.81	3.04	9.64	3.71	6.72	3.26
30	0.790	2.86	3.28	3.02	9.51	3.53	8.30	4.09
60	0.831	2.82	2.88	2.96	8.84	3.36	9.01	3.94
100	0.787	2.82	2.56	2.94	7.96	3.30	9.44	3.82
300	0.770	2.81	2.10	2.90	6.32	3.16	9.53	3.56
600	0.799	2.82	1.85	2.90	5.60	3.09	9.28	3.42
1000	0.810	2.74	1.84	2.82	5.11	3.04	8.90	3.32
2000	0.750	2.80	1.65	2.86	4.05	2.98	8.41	3.21
	SAMPLE 23, 28.41% COMBINED S							
0.600	0.362	3.07	1.10	3.22	5.63	3.58	7.31	4.59
0.960	0.275	3.07	1.02	3.20	5.19	3.53	7.73	4.48
2.160	0.293	3.07	0.906	3.18	4.28	3.46	7.80	4.26
13.5	0.366	3.09	0.751	3.11	3.54	3.32	8.86	3.88
30	0.499	3.12	0.779	3.16	3.18	3.34	8.51	3.73
60	0.464	3.06	0.769	3.14	2.83	3.31	7.71	3.70
100	0.482	3.06	0.815	3.13	2.72	3.26	6.99	3.53
300	0.574	3.06	0.778	3.13	2.17	3.24	5.49	3.40
600	0.620	3.07	0.819	3.14	1.99	3.20	4.90	3.34
1000	0.688	3.02	0.825	3.08	1.97	3.14	4.71	3.24
2000	0.525	3.03	0.772	3.09	1.75	3.14	4.30	3.22

[a] Power factor. [b] Dielectric constant.

Rise in temperature shifts the power factor maximum of a given compound toward higher frequency to a surprising extent. At constant frequency it shifts the maximum toward higher sulfur contents. A significant point is that, whereas low sulfur compounds are inherently materials of low power factor over the whole temperature and frequency ranges covered, the high sulfur compounds show low losses only at low temperature. At higher temperatures, hard rubber is a very poor dielectric. It is clear, therefore, that hard rubber is not intrinsically the electrically neutral material formerly supposed. Its good dielectric properties at room temperature

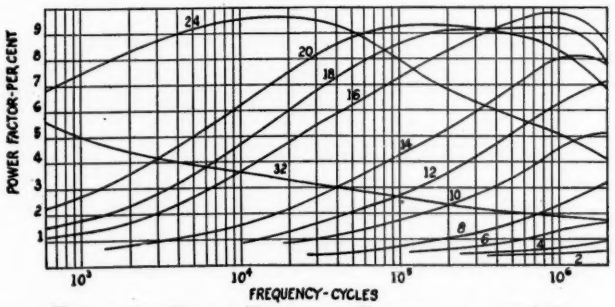

FIGURE 4. POWER FACTOR *vs.* FREQUENCY AT 75° C.

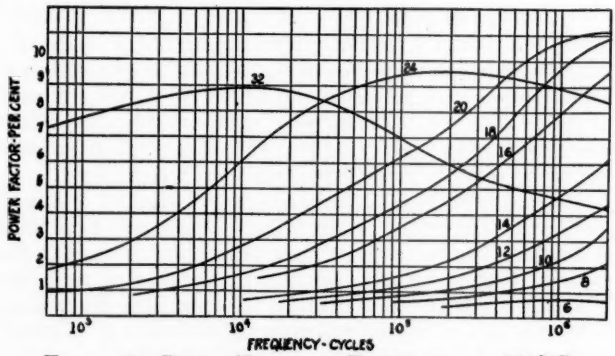

FIGURE 5. POWER FACTOR *vs.* FREQUENCY AT 100° C.

are due not to absence of the agents which produce high power factor and dielectric constant, but to their inability to respond when the material is sufficiently rigid. If a dipole mechanism is involved, the hard rubber molecules are certainly not compensated or electrically balanced. The misleading curve of static or d. c. dielectric constant *vs.* per cent sulfur will be more fully discussed later in the paper.

HIGH SULFUR RUBBER NOT ELECTRICALLY HOMOGENEOUS

The curves obtained by replotting the data for sample 16 in terms of the generalized dielectric constant (Figure 6) show some interesting features. These particular data were chosen

because they give curves conveniently located on the frequency scale.

The generalized dielectric constant is:

$$E = E' - iE''$$

where E' = ordinary dielectric constant
$i = \sqrt{-1}$
$E'' = E' \tan \phi$
where ϕ = phase difference
$\tan \phi = \omega C_x R_x$ or the expression used in Equation 1 for power factor

Practically therefore E'' = dielectric constant times power factor. Thus E is a complex quantity which involves both the dielectric constant and the energy losses.

From Debye's formulas (*4*) we derive the relations:

$$E' = \frac{E_0(E_\infty + 2)^2 + (f/f_0)^2 E_\infty (E_0 + 2)^2}{(E_\infty + 2)^2 + (f/f_0)^2 (E_0 + 2)^2} \qquad (3)$$

$$E'' = \frac{f/f_0 (E_0 - E_\infty)(E_\infty + 2)(E_0 + 2)}{(E_\infty + 2)^2 + (f/f_0)^2 (E_0 + 2)^2} \qquad (4)$$

where E_0 = dielectric constant at zero frequency
E_∞ = dielectric constant at infinite frequency
f = applied frequency
f_0 = characteristic frequency
$f/f_0 = \omega/\omega_0 = \omega T$, $\omega = 2\pi f$, T = relaxation time

By E_0 and E_∞ are meant the values at frequencies very low and very high, respectively, compared to f_0. As the E' observed curve shows, the frequency range from 600 to 2,000,000 cycles is too narrow to give either extreme, but, if we take the values at these points as E_0 and E_∞, respectively, substitute in Equations 3 and 4, and calculate E' and E'' at different intermediate frequencies, we can get a sufficient indication of how the experimental results follow the theory. For f_0, that frequency is taken which gives maximum power factor.

The maximum of E'' calculated is approximately double E'' observed. This ratio between the actual losses and those calculated from the drop in dielectric constant is about the same as that previously observed in the case of rosin (*9*). The author was unable at the time to explain the discrepancy but, when the calculated and observed curves for E' of rubber are compared, an explanation becomes possible.

The curve E' calculated represents the behavior of a material having a single relaxation time. The agents giving the drop, $E_0 - E_\infty$, are assumed to be all alike, so the whole drop takes place over a narrow frequency range. In this actual sample of rubber, on the other hand, there are present bodies of widely different relaxation times, and the drop in dielectric constant is, therefore, spread over a wide frequency range. This is shown by the slow, almost linear drop in E' observed. Each $\Delta E'$ due to bodies of a given relaxation time would be accompanied in the same frequency region by a corresponding loss or E'' value. The observed curves are the resultant of all the separate $\Delta E'$ and the corresponding E'' increments. The total losses summed up over the whole frequency range

would be equal to those calculated for a single type of body giving all the loss in a narrower frequency band, but of course the maximum value would be lower.

It should be pointed out that the equations for E' and E'' do not require a dipole mechanism, but hold for any mechanism in which the polarization possesses a relaxation time. Even a complete check between observed and calculated curves would not prove a dipole mechanism. Independent proof of dipoles would be required. On the other hand, the lack of agreement does not disprove the dipole concept, but merely shows

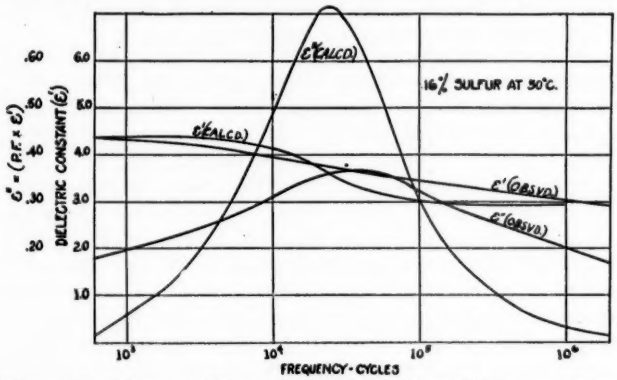

FIGURE 6. PLOT OF DATA FOR SAMPLE 16 IN TERMS OF GENERALIZED DIELECTRIC CONSTANT

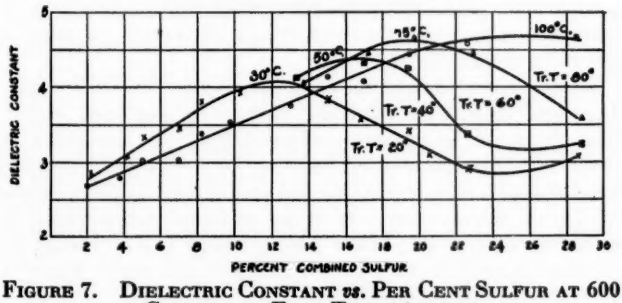

FIGURE 7. DIELECTRIC CONSTANT *vs.* PER CENT SULFUR AT 600 CYCLES AND FOUR TEMPERATURES

that, if dipoles are involved, they differ greatly among themselves in size. What these curves bring out is the wide range of relaxation times in high sulfur rubber, and hence its electrical inhomogeneity.

EFFECT OF TEMPERATURE

The influence of increased temperature in raising the power factor and the dielectric constant has been mentioned. Figure 7 in which the dielectric constant at 600 cycles is plotted *vs.* per cent combined sulfur at 30°, 50°, 75°, and 100° C. shows more clearly the influence on the dielectric constant. In the softer region from 0 to 12 per cent sulfur,

the dielectric constant for a given composition decreases with rising temperature as would be expected. In the high sulfur region the opposite effect occurs. At 28 per cent sulfur there is a marked increase in dielectric constant with temperature. Then, unless we make the improbable assumption that increase in temperature produces a pronounced chemical change in the rubber, the controlling influence must be the physical state of the material—i. e., whether it is hard or soft. In this respect rubber shows a certain similarity to viscous polar dielectrics (*8*, *9*). Over the range where sufficient softness permits free response, the dielectric constant increases almost linearly with combined sulfur content.

A significant relation can be shown between the dielectric behavior, as influenced by temperature, and certain other physical properties of vulcanized rubber. Adams and Gibson (*1*) have shown that soft rubber has the typical compressibility curve of a liquid, and hard rubber, that of a solid. Kimura and Namikawa (*7*) studied the thermal expansion over the whole combined sulfur range. Their curves of specific volume *vs.* temperature for samples of different sulfur content are all similar in shape, consisting of two straight lines joined by a relatively short curved portion. The coefficient of expansion, represented by the slope, does not vary uniformly with temperature over the whole temperature range, but over an interval of a few degrees changes from one constant value below the transition to about double above it. Since this change is not sharp, but is spread over several degrees, the two straight portions of the curve were continued and their intersection taken as the transition temperature in order to obtain a definite figure.

Figure 8, copied from the Japanese paper, shows the transition temperature so obtained plotted *vs.* per cent sulfur. The Japanese investigators showed that the transition in coefficient of expansion corresponds to a softening, because small samples clamped at one end just started to bend at the transition temperature. It is the softening temperature or pseudomelting point, below which rubber is in the hard or solid state, and above which it is in the soft state, where it resembles a viscous liquid.

The influence of temperature on the dielectric constant, though less abrupt, is similar. Figure 7 shows the effect. Transition temperatures taken from Figure 8 for 18, 20, 24, and 28 per cent sulfur, and denoted by *Tr.* *T.* = 20°, 40°, 60°, and 80° C., are placed on the corresponding coördinates between the curves of dielectric constant for the adjacent temperatures. So arranged, the data show that, while the dielectric constant rises with temperature even in the hard state, the most rapid increase occurs around the transition point. Above the transition temperature the dielectric constant first rises with temperature, passes through a maximum, and then falls again. This trend is clearly shown by the values for 18 and for 20 per cent sulfur at the several tempera-

tures. In the lower sulfur range the dielectric constant decreases only with rising temperature, but this is because here the test temperatures are far above the transition temperatures. This rise and fall of dielectric constant with increasing temperature shown by vulcanized rubber in the soft state is the behavior characteristic of viscous liquids (*8*, *9*). The fact that the dielectric constant does not drop immediately to the minimum value just below the transition temperature need not surprise us; for even in the case of water, which has a definite freezing point, the low-frequency dielectric constant does not drop suddenly to low values on solidification, but only at temperatures considerably below 0° C.

Thus the combined results of these studies reveal two distinct states in either of which, depending on the temperature, vulcanized rubber of a given sulfur content can exist: a hard state in which its behavior with respect to compressibility, rigidity, thermal expansion, dielectric constant, and power factor, and doubtless other properties, is like that of a solid; and a soft state in which it resembles a viscous liquid.

Discharge Time of Hard Rubber. Hard Rubber Not an "Electret"

According to the above reasoning the higher the combined sulfur content the higher the potential dielectric constant. By this is meant the high dielectric constant observed at sufficiently high temperature and low frequency to permit free response of the active agents. That a frequency of 600 cycles is too high to permit free response in hard rubber at room temperature is shown by the large difference in Figure 7 between the values for 28 per cent sulfur at 100° and 30° C. This suggests the question of how low the test frequency would have to be to give the high value at room temperature. The d. c. curve mentioned earlier in the paper also drops to low values in the high sulfur range. These so-called static values were obtained by discharge through a ballistic galvanometer with a period of the order of one second. Therefore, the dielectric constants so obtained are those for a frequency of the order of one cycle per second. This is still too high, and the curve of dielectric constant *vs.*

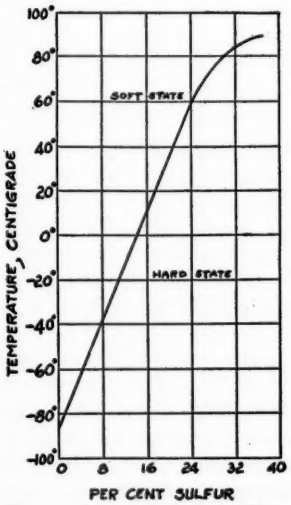

Figure 8. Softening Temperature *vs.* Composition

sulfur content, therefore, drops to low values in the high sulfur range.

This marked change in dielectric constant with temperature, considered with the softening phenomena studied by the Japanese investigators, suggested the idea than an "electret" might be made with hard rubber. An electret is the electrostatic analog of a permanent magnet. Certain mixtures of waxes cooled from the molten to the solid state under continuous electric stress maintain the polarization indefinitely (*5*). It was thought that hard rubber similarly cooled from the soft state at 100° C. to room temperature might be able to hold its charge for long periods.

To test this idea, two samples of hard rubber were prepared with 6-inch aluminum electrodes molded in. One was heated to 100° C. and allowed to cool overnight under a unidirectional stress of 3000 volts. It was then tested for charge after various periods of short circuit at room temperature. The electrodes were connected to a gold-leaf electroscope and

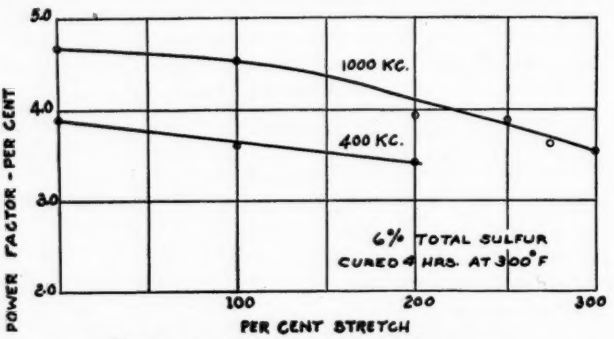

FIGURE 9. POWER FACTOR *vs.* STRETCH

the "frozen in" charge liberated by warming the sample. To detect minute residual charge at room temperature more delicate methods would be required. The uncharged sample was connected to the electroscope and heated in the same way as a blank and found not to be pyroelectric.

After a number of tests it was found that the longest time the sample would hold a charge detectable by this method after short circuit at room temperature was about 24 hours. At high temperature the charge was released instantly.

These tests showed that hard rubber does not become an electret as ordinarily defined, but a sort of quasi electret, since the difference is probably only one of degree. They show also that the agents responsible for the high dielectric constant at 100° C. are capable of responding even at room temperature, but very slowly. This was further proved by subjecting the sample to a 24-hour charge at room temperature. After such charge it showed the same results on test as the sample cooled under stress.

The large difference between this charge or discharge period

of 24 hours and the period of one second of the ballistic galvanometer accounts for the low dielectric constant at room temperature of high sulfur compounds by the so-called d. c. test.

Change in Power Factor of Rubber on Stretch

It has been shown by x-ray studies that when a piece of rubber is stretched an orientation takes place which gives rise to a longitudinal fibrous structure. This fibrous structure has also been visually demonstrated by Hock (*6*), who showed that stretched samples chilled in liquid air, on being struck, broke up into long fiber bundles, while an unstretched sample fractured like glass. It is assumed that the rubber molecules orient in long chains in the direction of stretch.

It seemed probable that the power factor would be affected by stretch; preliminary tests were therefore made to check this idea. A sheet of rubber containing 6 per cent total sulfur was cured 6 hours at 300° F. (148.9° C.) and tested at 500,000 cycles with the following results:

	Power Factor
	%
Unstretched	6.80
Stretched 150%	6.05
Released and tested immediately	6.77
Allowed to relax 30 minutes	6.81

The last two figures, unless the difference is due to error, show that the power factor does not return immediately to the original value, but that a period of recovery is needed for the molecules to return to the random distribution.

Figure 9 shows similar measurements at 400,000 and 1,000,000 cycles on a sample containing 6 per cent total sulfur cured 4 hours at 300° F. (148.9° C.).

This decrease in power factor is like the drop in dielectric constant with stretch discovered by Schiller (*10*) and is probably due to the same mechanism. A dipole mechanism is sufficient but not necessary to explain both effects. When the molecules are lined up by stretch, they are under constraint which restricts their response to an electric field, thereby decreasing power factor and dielectric constant. On the other hand, the behavior may be due merely to the fact that in stretched rubber the properties are different according as they are measured with or across the direction of stretch. It would be of great interest to measure power factor and dielectric constant in the direction of stretch, but this seems hardly practicable.

Conclusions

1. Power factor and dielectric constant data have been given for vulcanized rubber samples tested over a wide range of composition, temperature, and frequency.

2. The real identity of the agents responsible for the peculiar dielectric behavior is not known. It seems probable that these agents are the rubber-sulfur molecules themselves,

because the effects increase, under proper conditions, directly with per cent combined sulfur.

3. The effect of increasing sulfur content on the dielectric behavior is complex; it modifies not only these supposed agents themselves, but also the stiffness of their environment. Moreover, at a given sulfur content the agents are not identical but differ widely in relaxation time, and therefore in ability to respond; and with progressive addition of sulfur, the rubber does not increase continuously in stiffness, but, at a composition which depends on the temperature, passes rather abruptly from a soft to a hard state.

4. The temperature at which the transition from one state to the other occurs increases almost linearly with the sulfur content from $-90°$ to $+90°$ C.

5. In the soft state the behavior of vulcanized rubber with respect to compressibility, thermal expansion, dielectric constant, and power factor, and probably other properties, resembles that of a viscous liquid; in the hard state, that of a solid.

6. Rubber with less than 2 per cent combined sulfur shows low dielectric constant and power factor over the whole temperature and frequency range investigated; hard rubber, only at room temperature, where its rigidity restricts the response to the field.

7. Hard rubber, although not an electret, can hold an electric charge for 24 hours or more. The low dielectric constants of high-sulfur rubber samples found in measurements with a ballistic galvanometer were due to the disparity between its period of about one second and the long discharge periods of the samples. This led to the idea of dipole compensation shown to be incorrect by the high temperature results.

8. At temperatures sufficiently high to permit free response, the dielectric constant increases with sulfur content over the whole range.

9. If a dipole mechanism is involved, addition of sulfur to more than half the double bonds does not cause the dipole moment of the molecules to vanish owing to compensation.

10. The power factor of vulcanized rubber sheets decreases on stretch.

11. The data neither prove nor disprove a dipole mechanism. A critical experiment to settle this question is still wanting.

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Reactions during Vulcanization

II Reaction between Zinc Soaps and Mercaptobenzothiazole

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Fatty acids react rapidly with zinc oxide to form zinc soaps during milling, and accordingly the action of fatty acid in the presence of zinc oxide is the same as that of an equivalent amount of the corresponding zinc soap.

In accelerated stocks, the zinc soaps in the mix react with the accelerator to form the active zinc accelerator compound. The dynamic equilibrium between the accelerator and zinc soaps results in the formation of a smaller amount of the zinc accelerator compound in the case of mercaptobenzothiazole than for many accelerators, and accordingly relatively large amounts of zinc soaps are required with it.

Since the zinc reacts with mercapto benzothiazole as the zinc soap, and since there is sufficient time for the reaction between zinc oxide and the fatty acid to proceed to practical completion, irrespective of the particle size of the zinc oxide, it follows that particle size of the zinc oxide is not a factor in the activation of mercaptobenzothiazole.

AMONG the milestones of the past decade, marking increased knowledge regarding the activation of organic accelerators by zinc oxide, the work of Russell

(*9*, *10*) should be mentioned. He showed that it was desirable for the zinc to be in a form soluble in rubber, such as the zinc soaps of fatty acids. Bedford and Winkelmann (*3*) attacked the problem of the solubility of metallic substances as soaps from a somewhat different angle, using litharge and organic acids. They showed that fatty acid reacted with the lead oxide present in rubber and brought it into solution as the lead soap, in which condition it could act as a vulcanizing agent, and from which the lead could be precipitated as black lead sulfide by the hydrogen sulfide formed during vulcanization.

The reaction between zinc oxide and fatty acid is very rapid according to Whitby and Evans (*15*). They pointed out the extreme reactivity by stating that they shook 1.5 grams of stearic acid and 2.5 grams of zinc oxide in toluene (total volume 100 cc.), that 15 per cent of the stearic acid reacted at room temperature in 20 minutes, and that 96 per cent reacted in 40 minutes at the boiling point.

$$ZnO + \text{fatty acid} \longrightarrow \text{zinc soap} + H_2O$$

On the basis of these data it would be reasonable to expect that most of the fatty acid would have combined with zinc oxide during milling, and that zinc soaps added to the rubber would act the same as an equivalent amount of fatty acid and zinc oxide, irrespective of the particle size of the latter. Figure 1 illustrates by rubber tests that there is no difference in action between fatty acids in the presence of zinc oxide and the zinc soaps.

Lead oxide reacts the same as zinc oxide with fatty acids to form lead soaps and, in turn, lead compounds of the accelerators. The greater activation of zinc oxide containing free lead oxide in a mercapto[1] stock compared with pure lead oxide or pure zinc oxide might logically be explained on the basis of the formation of larger amounts of the lead and zinc accelerator compounds. There is an alternative, however, which may be discussed in a later paper of this series to the effect that lead oxide reacts with proteins naturally present in the rubber to form secondary accelerators.

Bedford and Gray (*2*) stated that the zinc compound of the organic accelerator was the true accelerator, and that it activated the sulfur in the mix. In order to bring out the full curing power, however, it was necessary to add additional zinc to the compound to replace the zinc precipitated as zinc sulfide by the hydrogen sulfide formed during vulcanization. They suggested that, when the zinc accelerator compound was decomposed by hydrogen sulfide, the zinc compound could be formed again by the accelerator migrating to a zinc oxide particle and reacting with it, or by the zinc in the form of a soluble soap migrating to the accelerator.

Sebrell and Vogt (*13*) gave additional evidence confirm-

[1] Mercaptobenzothiazole will be referred to hereafter in this paper as mercapto.

ing the chemical theory of the action of zinc oxide and emphasizing the role of resins as zinc oxide carriers.

Martin and Davey (*6*) showed that, when enough zinc oxide was present, no organic acid was necessary, an observation which is reasonable on a basis of the accelerator migrating to the zinc oxide surface and reacting with it.

Effect of Mercapto on Acceleration

The advent of mercapto (*12*) brought about a new problem in acceleration, since much larger quantities of fatty acids—that is, soluble zinc—were required than when the other commonly applied accelerators were used.

This paper is presented to suggest that a dynamic equilibrium exists between mercapto, its zinc compound, fatty acid, and zinc soap, in which the velocity of the reaction between the zinc soap and the mercapto is the same as the reaction rate between the zinc mercapto compound and the free fatty acid.

$$\text{Mercapto} + \text{zinc soap} \rightleftharpoons \text{zinc mercapto compound} + \text{fatty acid}$$

As the amount of fatty acid in the presence of zinc oxide and, accordingly, the zinc soap is increased, the reaction proceeds by mass action to the right until, with sufficient fatty acid, approximately 100 per cent of the mercapto is in the form of the zinc compound.

As suggested by Bedford and Gray (*2*) hydrogen sulfide reacts with the zinc soap and the zinc accelerator compound during vulcanization, and precipitates zinc sulfide, most of which probably comes from the zinc soap:

$$\text{Zinc soap} + H_2S \longrightarrow ZnS + \text{fatty acid}$$

Chemical analysis, as well as indirect evidence (*4*), shows that the amount of zinc sulfide formed increases as the amount of fatty acid in the compound increases.

In the case of accelerators other than mercapto the same equilibrium conditions probably apply, but, since the compounds of zinc oxide and the accelerators are generally more stable, much smaller excesses of zinc soaps are ordinarily necessary to form a large percentage of the active zinc accelerator compound.

Experimental Procedure

Since there were technical difficulties in the way of showing the equilibrium with rubber as a reaction medium, experiments were made approaching the equilibrium from one side, using a low-viscosity liquid from which the excess of zinc oxide could be filtered.

A solvent was made up containing 12.5 per cent of methanol and 87.5 per cent of benzene. To this solvent, U. S. P. zinc oxide, mercapto, and fatty acid from coconut oil were added so that 100 cc. contained 8 grams of zinc oxide, 2 grams of mercapto, and increasing amounts of coconut oil fatty acids, ranging from 0 to 2 grams. After standing with occasional stirring for

16 hours at 50° C., the clear solution was filtered off, evaporated, and ignited to determine the amount of soluble zinc as the oxide. It was necessary to filter hot to hold the zinc soaps in solution, and the method appeared unreliable when the amount of added fatty acid exceeded 1 gram, owing to the relatively low solubility of the soaps.

Discussion of Results

The data in Table I show that there is practically no reaction between solid zinc oxide and mercapto. Accordingly, in an acetone-extracted rubber, no cure is to be expected using mercapto and zinc oxide without adding organic acid, a result which agrees with general experience. From the extrapolated data plotted (Figure 2), it will be seen (assuming no adsorption of accelerator or fatty acid) that a minimum of about 1.5 grams of fatty acid from coconut oil or 2.1 grams of the equivalent longer-chain fatty acid are necessary to bring out the full curing power of mercapto.

Table I. Equilibrium between Mercapto and Zinc Soaps

Acid Added in 100 cc.	Sol. ZnO Found in 100 cc.	Calcd.[a] ZnO Combined with Fatty Acid	Calcd. ZnO Combined with 2 Grams of Mercapto	Mercapto[b] Present as Zinc Salt
Gram	*Gram*	*Gram*	*Gram*	%
0.0	0.0220	0.0000	0.0220	4.5
0.1	0.1353	0.0205	0.1148	23.7
0.3	0.2379	0.0615	0.1764	36.5
1.0	0.6036	0.2050	0.3986	82.5

[a] The zinc soap contains 17 per cent of ZnO, and an error of even 2 per cent in this figure would not greatly modify the calculation.

[b] The molecular weight of mercapto is 167 and of ZnO, 81. The combining ratio is 334 of mercapto to 81 of ZnO.

The equilibria may, of course, be somewhat different at vulcanizing temperatures than at 50° C., at which temperature these experiments were carried out, but the general conclusions should not be changed.

The conclusions in reference to the equilibrium would be more conclusive if the equilibrium could be approached from the zinc mercapto side, and with this thought, Steele (*14*) has suggested the possibility that the action of the zinc soaps in forming the zinc accelerator compound may be an effect on the velocity of reaction rather than a true equilibrium. The published data (*13*) showing that the zinc compound of mercapto is ineffective in extracted rubber may be used as an argument against this suggestion and in favor of the equilibrium theory. The zinc compound of mercapto is unstable and breaks down, forming the inactive mercapto.

Although it was convenient to use a 12.5 per cent solution of methanol in benzene to study the reaction quantitatively, the reaction can be shown qualitatively in the case of rubber. Neglecting the relatively small amount of fatty acid present in the rubber, the heavy line, *B* (Figure 3), represents a condition in which there is just enough zinc oxide to combine with all the fatty acid. Adding more fatty acid, as in *A*, causes the equilibrium to move to the left and the cure to

proceed more slowly. When the fatty acid content is decreased, as in *C*, the rate of cure increases because the equilibrium moves to the right with the formation of more of the zinc mercapto compound, precipitation of zinc by hydrogen sulfide generating an excess of fatty acids. As the amount of fatty acid (and therefore zinc soap) is further decreased, the amount of the zinc mercapto compound decreases, and the rate of cure slows down again, as in *D*.

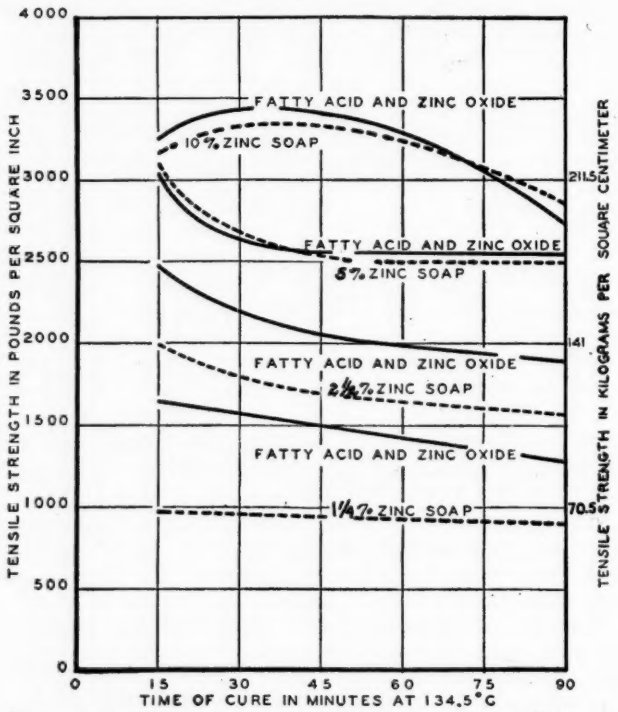

Figure 1. Comparison of Curing Properties of Rubber Compounded with Zinc Soap and Equivalent Amount of Fatty Acid and Zinc Oxide

Formula	
Pale crepe	100
Sulfur	3
Mercapto	1
Zinc soap (or equivalent of zinc oxide and fatty acids from cocoanut oil)	1.25–10

Similarly, when more zinc oxide is added, the rate of cure increases, since there is a reservoir of zinc oxide to replace that precipitated as zinc sulfide and to maintain the fatty acid in the form of the zinc soap; both increasing the concentration of zinc soap and decreasing the amount of fatty acid tend to increase the amount of the zinc mercapto compound, the effective accelerator which reacts with sulfur to furnish it in an available form.

The equilibrium described in this paper is not unique;

an equilibrium in the case of dithiocarbamates has been discussed (*5*), but in this case the zinc and lead compounds were relatively stable.

Considering this problem from a different angle, Aultman (*1*) has offered confirmatory evidence for the theory presented. He found that oleic acid added to a mercapto cement retards its set-up as required by the theory. The determination of equilibrium constants would be a decided step forward, and the method of using cements, to which definite amounts of soaps and fatty acids can be added, offers a promising method for obtaining these data.

The law of mass action is the fundamental law of general chemistry, and the application of this law to a study of the equilibrium between mercapto and zinc soaps rests on the chemical theory for the action of fatty acids in rubber which has been accepted by Bedford, Whitby, Sebrell, and others who have been quoted. The chemical theory has not been accepted by all investigators, however. Martin and Davey (*6*) published an article to show that the purpose of the fatty acid was to disperse the zinc oxide more completely, and later Davey (*4*) published another article adhering to the original contention and stating that the fatty acid was also necessary to disperse mercaptobenzothiazole. His case was well enough presented so that it was considered plausible by a number of rubber technologists (*11*).

Disadvantages of Dispersion Theory

Since a chemical equilibrium explanation has been advanced in this paper that is completely at variance with the dispersion theory, it is desirable to present the reasons for rejecting the dispersion explanation.

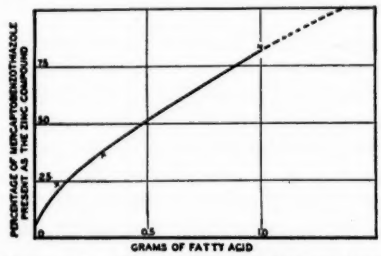

Figure 2. Influence of Fatty Acid on Equilibrium between Mercapto and Zinc Salt of Mercapto

First, in the case of litharge, Martin and Davey accepted the chemical explanation which was strengthened by the work of Reece (*8*), who studied the reactions between lead oxide and fatty acid and discussed the possibility of following the reaction by means of the water evolved. It would seem that inasmuch as both zinc oxide and lead oxide activate accelerators, if a chemical explanation is accepted for lead oxide, an unusual burden of proof should be required to justify a different explanation for zinc oxide.

Secondly, microscopic evidence has shown that zinc oxide disperses well in extracted rubber and that fatty acid is not

necessary to disperse it. An available series of observations on the three compounds listed in Table II are shown in Table III. Of the three compounds, R, containing rubber deficient in fatty acid, is shown to contain the largest number of zinc oxide particles well dispersed, whereas compound P, with fatty acid added, contains the smallest number owing to dissolution of some of the particles. If the reaction were a surface one and depended on the number of dispersed particles of zinc oxide, it would be expected that R would cure most quickly and P most slowly. The data in Figure 4 show the reverse to be the case, thereby indicating that soluble zinc soaps rather than dispersed zinc oxide particles are necessary.

TABLE II. ANALYSIS OF COMPOUNDS

	P Acid Added	Q Normal Rubber	R Deficient Rubber
Pale crepe	100	100	...
Rubber deficient in fatty acid[a]	...	...	100
Fatty acid from coconut oil	4.1	...	...
Sulfur	3.0	3.0	3.0
Zinc oxide (XX Red 65)	0.87	0.87	0.87
Mercapto	1.0	1.0	1.0

[a] Contains 40% as much fatty acid as is contained ordinarily in first quality rubber.

TABLE III. APPEARANCE OF COMPOUNDS FROM TABLE II

Compound	Macroscopic		Microscopic	
	Uncured	Cured	Uncured	Cured
P	Translucent	Transparent	Many zinc oxide particles well dispersed	No zinc oxide particles
Q	Semi-translucent	Transparent	Very many zinc oxide particles well dispersed	No zinc oxide particles
R	Opaque	Translucent	Extremely large number of well-dispersed particles	Many zinc oxide particles well dispersed

Third, following this same line of thought, since the zinc oxide of fine particle size (Kadox) can be dispersed reasonably well in rubber, and since the average particle size is only about half that of ordinary zinc oxide (XX Red), which calculates to eight times as many particles for the fine zinc oxide as for the ordinary zinc oxide, it would be expected that a considerably smaller amount of the finer zinc oxide would be needed for activation, whereas commercial experience has shown that a smaller amount is impractical.

Fourth, with reference to the statement that fatty acid is needed to disperse mercapto, microscopic tests have shown that mercapto dissolves in rubber (both normal and deficient in fatty acid) on heating, making the rubber transparent. The solubility (7) of mercapto at room temperature is less than 1 per cent, and accordingly, if the amount present is 1 per cent or above, like sulfur it will crystallize out on cooling. It usually crystallizes out in rods, some of which have pointed ends, and it occasionally crystallizes in dendritic forms. Although fatty acids have been observed to affect the solu-

bility of mercapto in some organic solvents, they do not appear to greatly affect its solubility in rubber, as shown by microscopic observations.

It has been found desirable to present evidence refuting

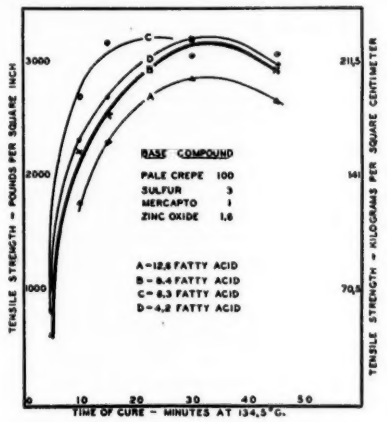

FIGURE 3. INFLUENCE OF FATTY ACID CONTENT ON RATE OF CURE OF MERCAPTO STOCKS

(The zinc oxide used for Figures 3 and 4 was Black Label Kadox, and the fatty acid came from coconut oil. It contains considerable ularic acid.)

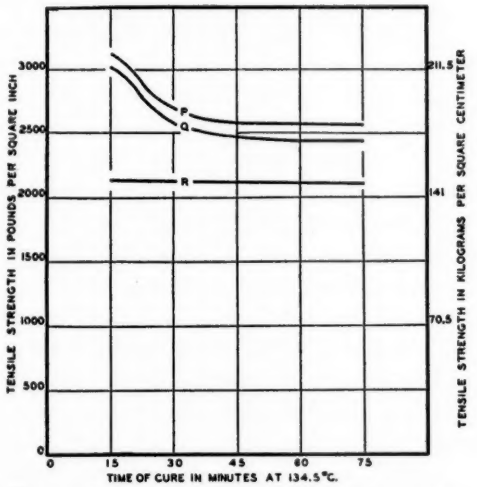

FIGURE 4. CURING CURVES FOR COMPOUNDS DESCRIBED IN TABLE II

the dispersion explanation of the action of zinc oxide during vulcanization, but the chemical theory does not stand on this negative evidence. Rather, the chemical explanation depends on the evidence presented earlier in this paper to

the effect that the curing properties of a mercapto stock depend on the amount of the zinc accelerator compound present, which is in equilibrium with zinc soaps and fatty acid, the latter being unable to exist in any appreciable concentration as long as free zinc oxide is present. Therefore, within limits an increase in the amount of fatty acid when an excess of zinc oxide is present results in an increase in rate of cure.

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Presented before the Meeting of the Rubber Division of the American Chemical Society, Detroit, Mich., February 25 and 26, 1932. The author's present address is American Zinc Sales Co., Columbus, Ohio.

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Effect of Cadmium Compounds on Typical Organic Accelerators during Vulcanization

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Cadmium may occur in zinc oxide in the form of oxide, hydroxide, sulfate, sulfide, chloride, and carbonate in quantities up to 0.5 per cent or slightly more. Using 10 parts of zinc oxide which contains 0.5 per cent of cadmium, the latter would not exceed 0.05 part on the rubber.

Owing to testing inaccuracies and the masking effect of impurities, small amounts of cadmium may be difficult to detect. To eliminate such complications, a base formula was selected using chemically pure zinc oxide to which were added various amounts of cadmium compounds. With few exceptions, these compounds retard tetramethylthiouram monosulfide but slightly advance the rate of cure of butyraldehyde aniline, diorthotolylguanidine, and mercaptobenzothiazole.

General analytical practice is insufficient to identify the various forms of cadmium present, and the action of cadmium-bearing zinc oxides is difficult to predict. Samples of three experimental zinc oxides gave widely different results with tetramethylthiouram

monosulfide. Two samples of comparatively low cadmium content assayed approximately the same. One was fast- and the other slow-curing; the third, assaying appreciably more cadmium, produced an intermediate rate of cure.

THE literature contains considerable information regarding the reactions of zinc oxide with thiouram accelerators. Some ten years ago Bedford and Sebrell (*1*) published a mechanism for the reaction of zinc oxide and tetramethylthiouram disulfide. Simmons and Cummings (*4*) showed that the monosulfide and disulfide were very similar in their action with zinc oxide. Recently Jones and Depew (*3*) have shown the influence of lead, and Bridgewater (*2*) gives data showing the influence of certain cadmium compounds. All of these explanations are dependent upon the formation of hydrogen sulfide during vulcanization and the formation of inert metallic compounds of the thiourams.

For some time it has been known that certain cadmium compounds effectively retard tetramethylthiouram monosulfide at various curing temperatures. A similar investigation of other typical accelerators disclosed the fact that all accelerators are not so affected. In some cases distinct acceleration results.

It is not the purpose of this paper to explain, at this time, the reactions of cadmium compounds with these accelerators but merely to present the data obtained.

The presence of cadmium in zinc ores is not at all uncommon and in pyrometallurgical processes it is volatile at lower temperatures than zinc, which makes possible practically 100 per cent recovery of the cadmium with zinc metal or zinc oxide. Cadmium may be removed from zinc ores by special treatment to produce zinc metal or oxide which is substantially cadmium-free.

In the commercial production of zinc oxide from cadmium-bearing metallic zinc (French process) or cadmium-bearing ores (American process), it is possible for many cadmium compounds to be present, but those most likely to occur are the oxide, hydroxide, sulfate, sulfide, chloride, and carbonate. In French process zinc oxide, the preponderance of cadmium is usually present as the oxide; in American process, as the oxide or sulfate, though it is possible for all six compounds to occur, depending upon operating conditions and procedure.

Experimental Procedure

Since metallic compounds other than cadmium may be present in commercial zinc oxides and have various effects on accelerators, C. P. zinc oxide (dry process) was used to eliminate any such possibilities.

Various amounts of cadmium compounds were incorporated in the batch. It is quite probable that such a method does

not typify the dispersion of cadmium compounds found in commercial zinc oxides, where the various metallic substances are most intimately associated with the zinc oxide, but it is sufficient to indicate their respective activities.

The various quantities of cadmium compounds used in this investigation are not, in every case, necessarily those most

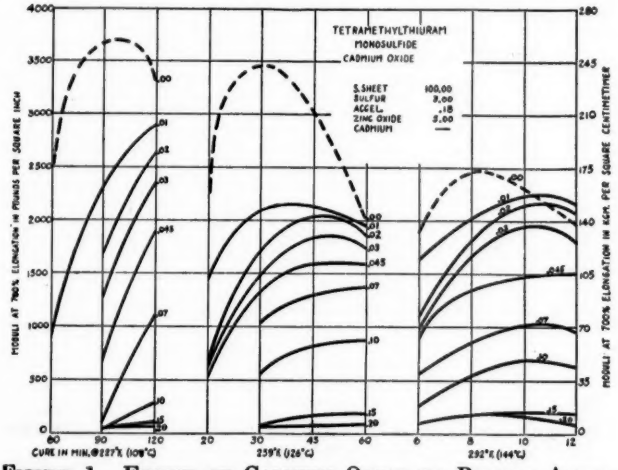

FIGURE 1. EFFECT OF CADMIUM OXIDE ON RUBBER ACCELERATED WITH TETRAMETHYLTHIOURAM MONOSULFIDE

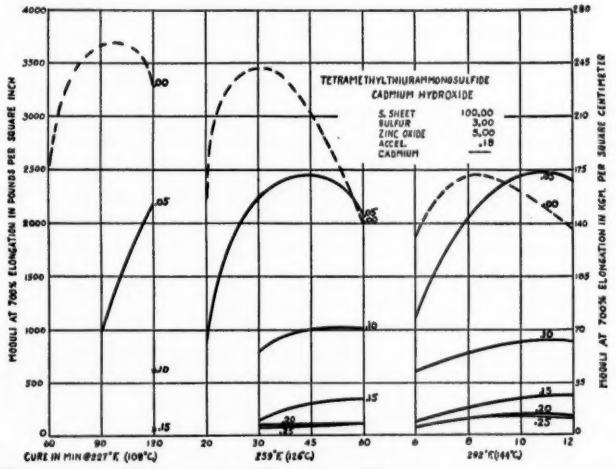

FIGURE 2. EFFECT OF CADMIUM HYDROXIDE ON RUBBER ACCELERATED WITH TETRAMETHYLTHIOURAM MONOSULFIDE

probable in cadmium-bearing zinc oxide. In some instances, comparatively large quantities were selected because certain compounds impart only a slight influence on rate of cure, and it was necessary to use excessive amounts to show their true characteristics.

Since gum stocks give more or less erratic tensile results, the curves presented in this paper are those representative of the moduli at 700 per cent elongation, which is near the breaking point.

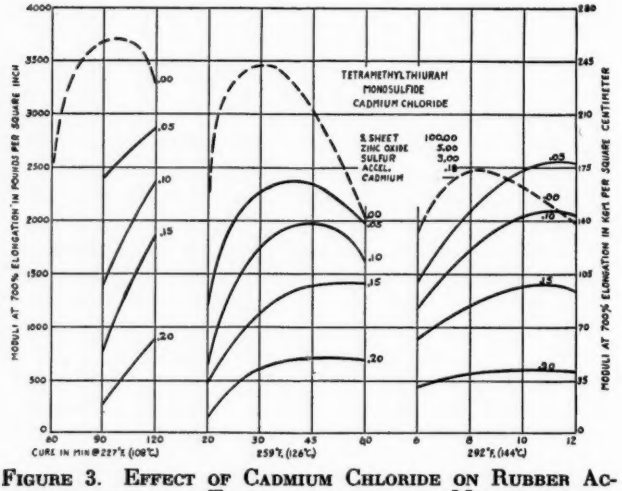

FIGURE 3. EFFECT OF CADMIUM CHLORIDE ON RUBBER ACCELERATED WITH TETRAMETHYLTHIOURAM MONOSULFIDE

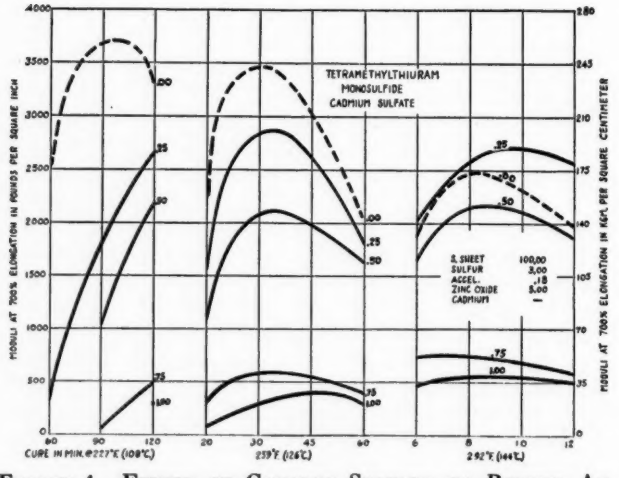

FIGURE 4. EFFECT OF CADMIUM SULFATE ON RUBBER ACCELERATED WITH TETRAMETHYLTHIOURAM MONOSULFIDE

TETRAMETHYLTHIOURAM MONOSULFIDE

The first accelerator investigated was tetramethylthiouram monosulfide, and various amounts of cadmium compounds were added to the following basic formula:

Rubber	100
Zinc oxide, C. P.	5
Sulfur	3
Tetramethylthiouram monosulfide	0.18

Figure 1 presents a comparison of the effects of various amounts of cadmium oxide ranging from 0.01 to 0.20 part on the rubber, which shows this ingredient to be an effective retardant at low curing temperatures. When the tempera-

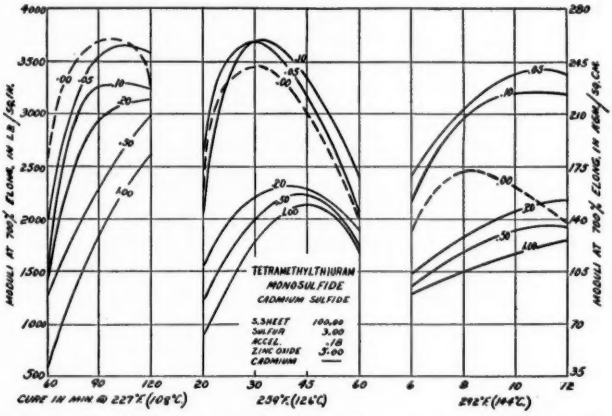

FIGURE 5. EFFECT OF CADMIUM SULFIDE ON RUBBER ACCELERATED WITH TETRAMETHYLTHIOURAM MONOSULFIDE

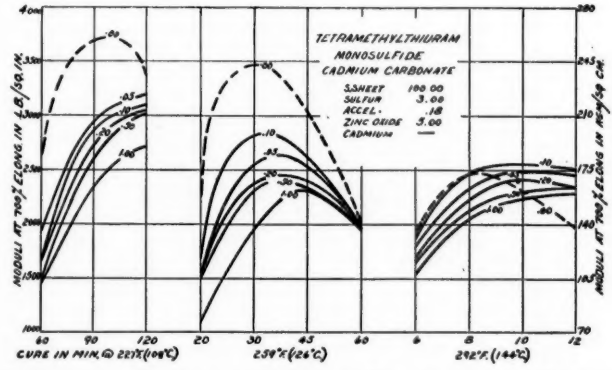

FIGURE 6. EFFECT OF CADMIUM CARBONATE ON RUBBER ACCELERATED WITH TETRAMETHYLTHIOURAM MONOSULFIDE

ture is raised to 292° F. (144° C.), the retarding action is considerably lessened, and fairly good cures result in 10 and 12 minutes with 0.01, 0.02, and possibly 0.03 part.

The results obtained with cadmium hydroxide and cadmium chloride (Figures 2 and 3) are somewhat similar. It will be noted, however, that larger amounts of these compounds were used than in the case of cadmium oxide since there were reasons to believe, when this work was undertaken,

that these compounds would not be as effective and that their presence in zinc oxide is more or less theoretical.

The presence of cadmium sulfate in zinc oxide is permissible in appreciable quantities as shown in Figure 4. Retardation develops at 227° F. (108° C.) when 0.25 part is

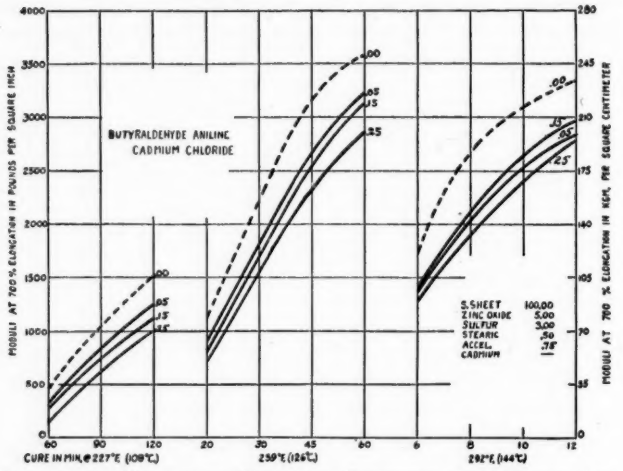

FIGURE 7. EFFECT OF CADMIUM CHLORIDE ON RUBBER ACCELERATED WITH BUTYRALDEHYDE ANILINE

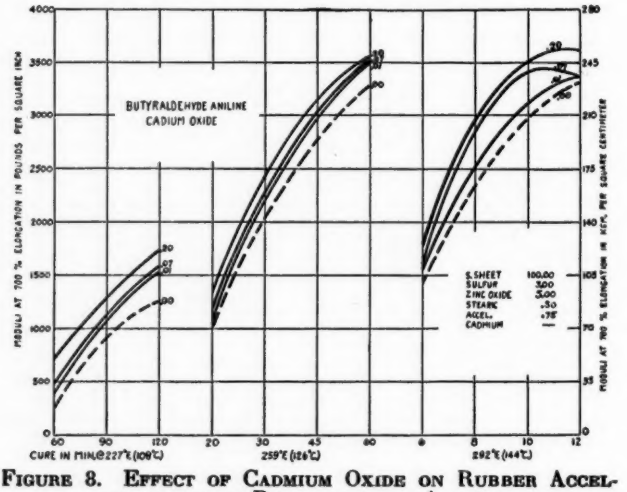

FIGURE 8. EFFECT OF CADMIUM OXIDE ON RUBBER ACCELERATED WITH BUTYRALDEHYDE ANILINE

used, but the effect is slightly less noticeable when the temperature is raised to 259° F. (126° C.) Not only is this amount inactive at 292° F. (144° C.), but it has a tendency to prolong the range of cure. When the cadmium sulfate content is increased to 0.50 part, a stock only slightly slower than the control is produced.

Another interesting form of cadmium is the sulfide, as illustrated in Figure 5. Small amounts show only slight retardation at 227° F. (108° C.), and at 259° F. (126° C.) the presence of 0.05 and 0.10 part has not affected the cure to any appreciable extent. Larger amounts, however, show marked

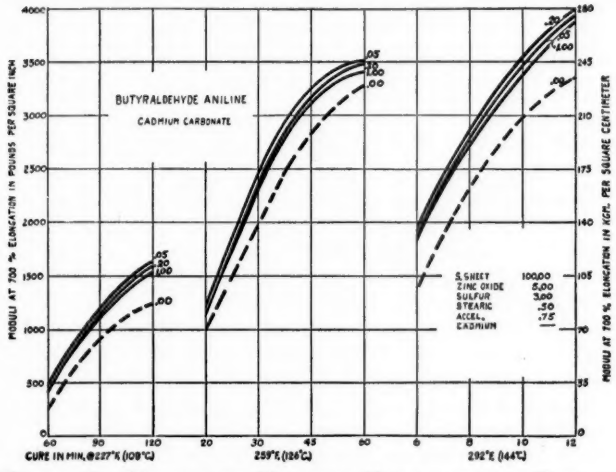

Figure 9. Effect of Cadmium Carbonate on Rubber Accelerated with Butyraldehyde Aniline

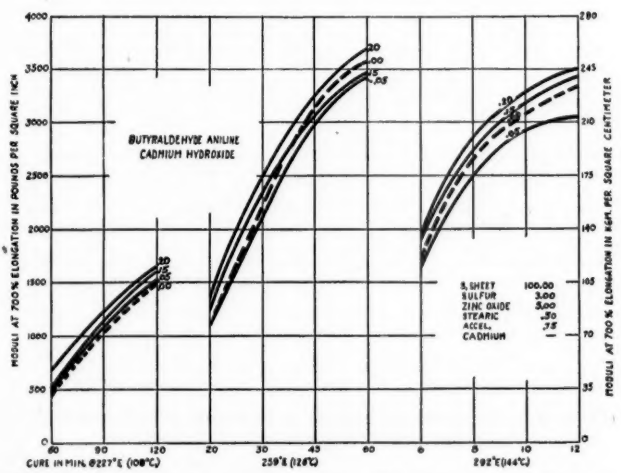

Figure 10. Effect of Cadmium Hydroxide on Rubber Accelerated with Butyraldehyde Aniline

retardation. When the temperature is raised to 292° F. (144° C.) this cadmium compound apparently activates tetramethylthiouram monosulfide, since 0.05 and 0.10 part produce considerably higher moduli and lengthen the range of cure.

Cadmium carbonate imparts retardation at 227° F. (108° C.) and 259° F. (126° C.), and the amount present is not very important, since 0.05 is almost as effective as 1.00 part (Figure 6). Although retardation is less noticeable at 292° F. (144° C.), the carbonate has a marked tendency toward flattening the curing range.

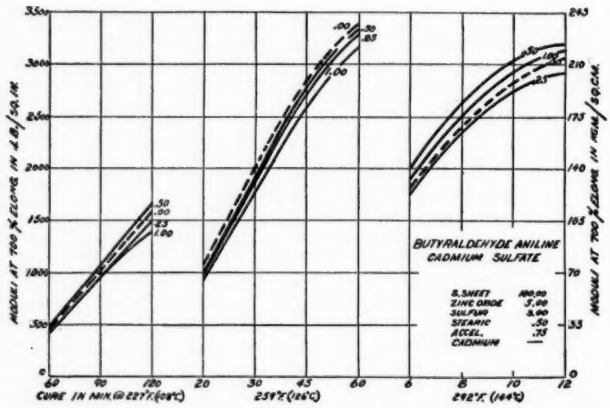

FIGURE 11. EFFECT OF CADMIUM SULFATE ON RUBBER ACCELERATED WITH BUTYRALDEHYDE-ANILINE

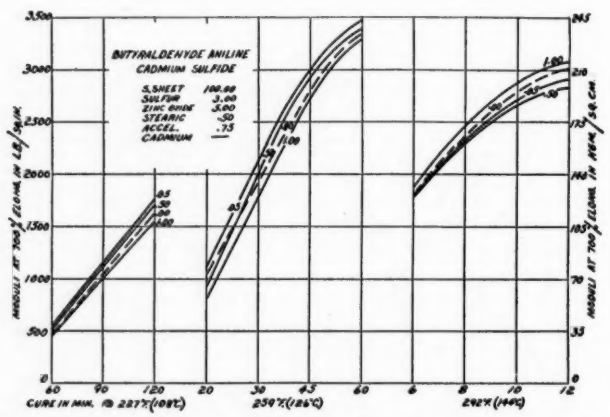

FIGURE 12. EFFECT OF CADMIUM SULFIDE ON RUBBER ACCELERATED WITH BUTYRALDEHYDE-ANILINE

BUTYRALDEHYDE ANILINE

A similar procedure was followed with an accelerator of the aldehyde-aniline type using the following formula:

Rubber	100.0
Zinc oxide, C. P.	5.0
Stearic acid	0.5
Sulfur	3.0
Butyraldehyde-aniline	0.75

A rather effective retarding agent at any temperature is found in the case of cadmium chloride, and the degree of retardation is directly proportional to the amount used (Figure 7).

It is well known that certain acid radicals influence the curing properties of some accelerators and it is possible that the presence of the chloride may be responsible for the action

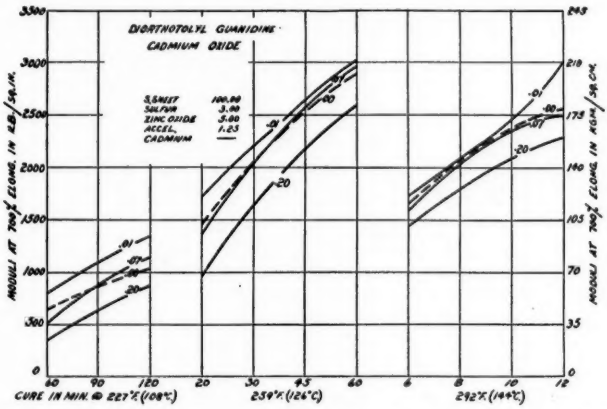

FIGURE 13. EFFECT OF CADMIUM OXIDE ON RUBBER ACCELERATED WITH DI-*o*-TOLYLGUANIDINE

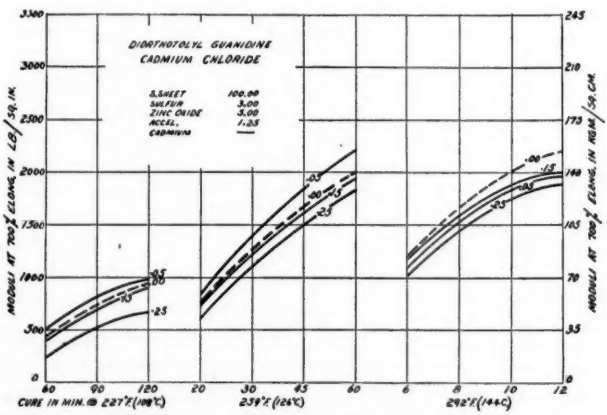

FIGURE 14. EFFECT OF CADMIUM CHLORIDE ON RUBBER ACCELERATED WITH DI-*o*-TOLYLGUANIDINE

noted, but the scope of this paper does not include other metallic chlorides.

Figures 8 and 9 represent the data obtained with cadmium oxide and cadmium carbonate which are apparently very similar in their activity. Both of these compounds produce higher moduli than the control stock at all three temperatures, and the various quantities used do not seem to influence the results to any appreciable extent.

Regardless of the quantities or curing temperatures used, cadmium hydroxide, sulfate, and sulfide gave practically the same characteristic results which do not vary materially from those obtained for the control stock, as shown in Figures 10 to 12.

Diorthotolylguanidine

The behavior of cadmium compounds with this accelerator is very interesting since their influence is rather pronounced.

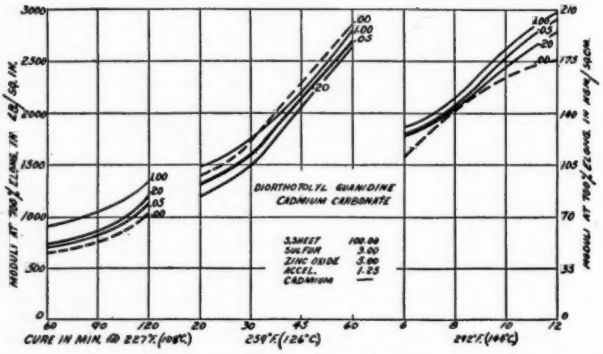

Figure 15. Effect of Cadmium Carbonate on Rubber Accelerated with Di-o-tolylguanidine

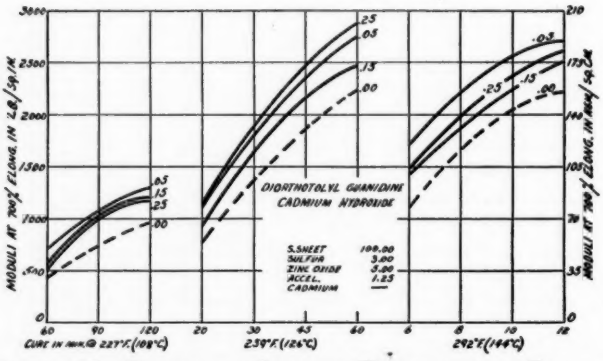

Figure 16. Effect of Cadmium Hydroxide on Rubber Accelerated with Di-o-tolylguanidine

Maintaining much of the same type of cure, the following formula was selected:

Rubber	100.0
Zinc oxide, C. P	5.0
Sulfur	3.0
Diorthotolylguanidine	1.25

Cadmium oxide is effective at all temperatures as represented in Figure 13. Quantities as small as 0.01 part produce definite acceleration. When the quantity is increased to 0.07

part, the results approximate those of the control, while larger amounts definitely retard.

Action of the chloride is similar to that of the oxide as shown in Figure 14.

The carbonate is another peculiar cadmium compound, inasmuch as the wide range of quantities used produces cures at 259° F. (126° C.) showing only slight retardation as represented in Figure 15. At 227° F. (108° C.) and 292° F. (144° C.) this compound develops definite activation.

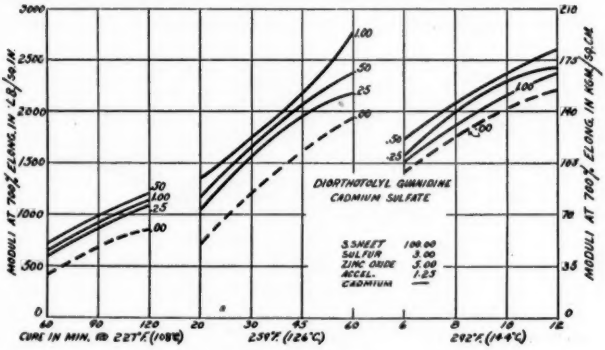

FIGURE 17. EFFECT OF CADMIUM SULFATE ON RUBBER ACCELERATED WITH DI-O-TOLYLGUANIDINE

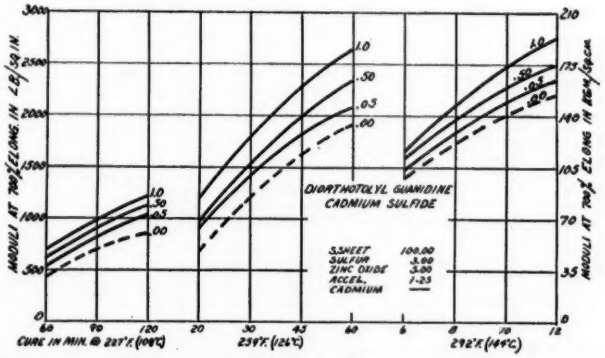

FIGURE 18. EFFECT OF CADMIUM SULFIDE ON RUBBER ACCELERATED WITH DI-O-TOLYLGUANIDINE

Of the six cadmium compounds tested with this accelerator, the hydroxide, sulfate, and sulfide show marked activation, although the data do not indicate that the effect is proportional to the quantities used (Figures 16 to 18). A larger number of determinations, no doubt, would establish a definite relation regarding quantity and activation.

MERCAPTOBENZOTHIAZOLE

Using the following formula, the data show that this type of accelerator is activated by certain cadmium compounds and

retarded by others, but the amounts necessary to produce retardation are considerably in excess of those most commonly present in zinc oxide:

Rubber	100
Zinc oxide, C. P.	5
Stearic acid	1
Sulfur	3
Mercaptobenzothiazole	1

Perhaps the most effective retarding cadmium compound is the chloride, as shown in Figure 19.

As previously mentioned, the larger amounts used in this work are considerably in excess of those commonly found in

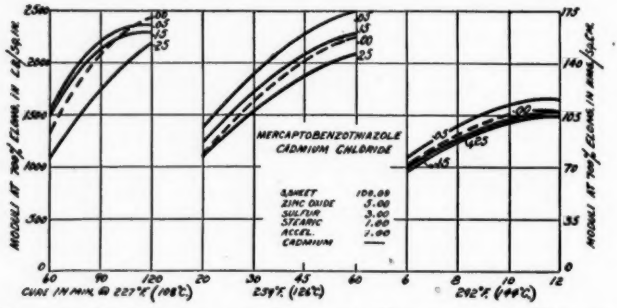

FIGURE 19. EFFECT OF CADMIUM CHLORIDE ON RUBBER ACCELERATED WITH MERCAPTOBENZOTHIAZOLE

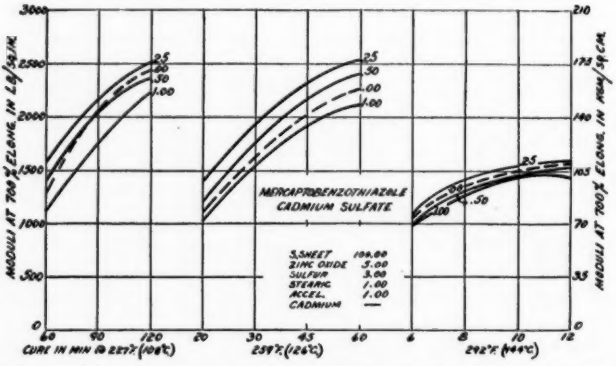

FIGURE 20. EFFECT OF CADMIUM SULFATE ON RUBBER ACCELERATED WITH MERCAPTOBENZOTHIAZOLE

zinc oxide. The smallest quantity used—0.05 part—activates this accelerator at all temperatures, and 0.15 part apparently has little effect. When the quantity is increased to 0.25 part, retardation is noted at 227° F. (108° C.) and 259° F. (126° C.), but the effect is scarcely noticeable at 292° F. (144° C.).

In Figure 20 the activation of cadmium sulfate is very slight at 227° F. (108° C.) and 292° F. (144° C.) when 0.25 part is present, and larger amounts (0.50 and 1.00 part) fail to impart marked retardation.

At 259° F. (126° C.) the effect of various amounts of cadmium sulfate is more pronounced. The smallest addition of 0.25 part produced appreciable activation, double the quantity continued to show a tendency toward activation, and it was necessary to increase the quantity four times before definite retardation developed.

In the case of cadmium sulfide, a wide range of additions was used as indicated in Figure 21. With the exception of 1.0 part cured at 227° F. (108° C.) where retardation occurred, this compound of cadmium apparently has little influence on the accelerator.

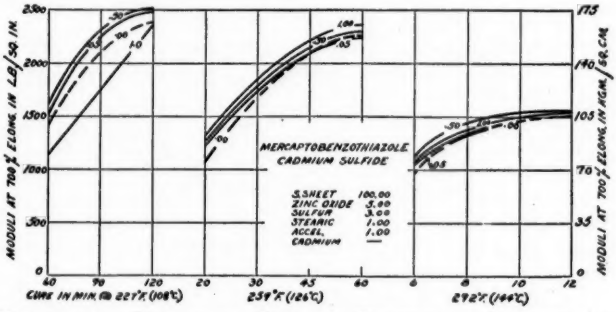

FIGURE 21. EFFECT OF CADMIUM SULFIDE ON RUBBER ACCELERATED WITH MERCAPTOBENZOTHIAZOLE

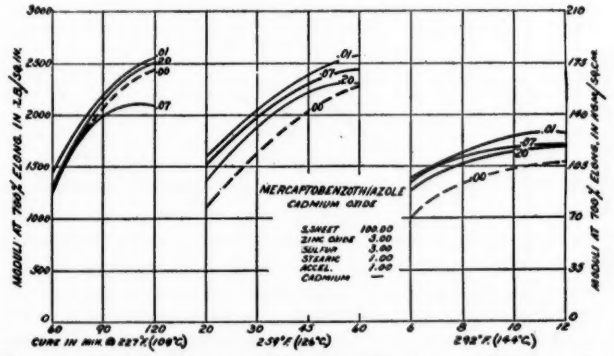

FIGURE 22. EFFECT OF CADMIUM OXIDE ON RUBBER ACCELERATED WITH MERCAPTOBENZOTHIAZOLE

The last three cadmium compounds investigated (oxide, hydroxide, and carbonate) produced much the same type of curves, although the additions of these compounds are not identical in each case.

Amounts of cadmium oxide ranging from 0.01 to 0.20 part do not influence cure at 227° F. (108° C.), as shown in Figure 22. At higher temperatures—259° F. (126° C.) and 292° F. (144° C.)—similar amounts develop marked activation, the magnitude being inversely proportional to the amount used. This is especially noticeable at 259° F. (126° C.). In Figures

23 and 24, cadmium hydroxide and carbonate are represented as being very similar in their activity. At 227° F. (108° C.) the activity of these compounds corresponds to that of the oxide, since all three are practically inactive at this temperature. Unlike the oxide at 259° F. (126° C.) and 292° F. (144° C.), the hydroxide and carbonate have approximately the same effect, regardless of the quantity used.

Discussion

The preceding information has shown many possible combinations of cadmium compounds and accelerators. Some

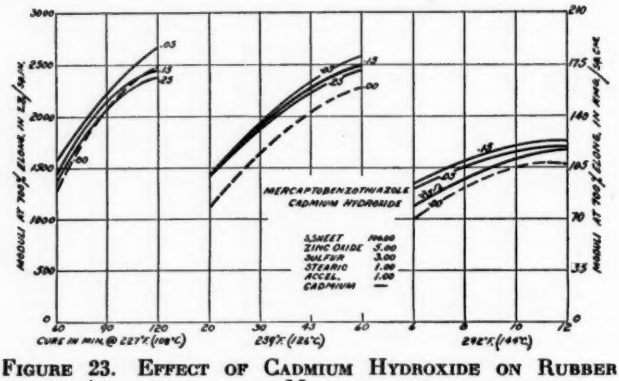

Figure 23. Effect of Cadmium Hydroxide on Rubber Accelerated with Mercaptobenzothiazole

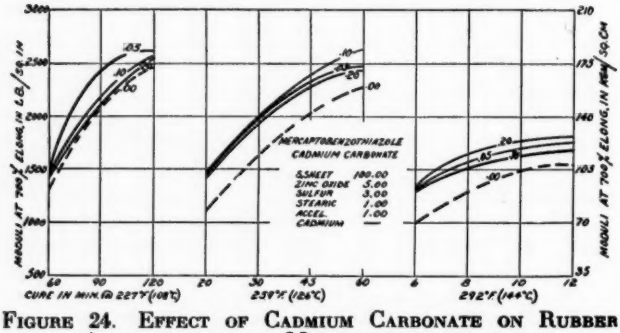

Figure 24. Effect of Cadmium Carbonate on Rubber Accelerated with Mercaptobenzothiazole

have been found to be practically inactive, others cause retardation, while a third group increases rate of cure.

To predict the action of cadmium-bearing zinc oxides in stocks would be very desirable and can be determined when the cadmium compounds present are identified accurately. General analytical practice in assaying zinc oxide separates the cadmium compounds into either of two groups—soluble or insoluble in water. The former includes sulfate and chloride, while the oxide, hydroxide, sulfide, and carbonate are insoluble, and identification of these compounds is not readily accomplished.

Figure 25 presents the data obtained with three experimental zinc oxides which gave the following assays:

	Sample A	Sample B	Sample C
Cd insoluble in H_2O	0.12	0.11	0.37
Cd soluble in H_2O	0.08	0.07	0.17
Soluble Zn as $ZnSO_4$	0.22	0.20	0.55
Total S	0.07	0.06	0.27
Pb as $PbSO_4$	0.04	0.04	0.04
Total H_2O-soluble	0.44	0.37	0.99
Acidity	0.06	0.09	0.07

Each sample was tested in a formula containing a commercial loading of zinc oxide:

Rubber	100
Zinc oxide	60
Sulfur	3
Tetramethylthiouram monosulfide	0.25

The above assays indicate that samples A and B compare very favorably regarding their cadmium content, but that the physical results obtained show a wide difference in their activity. At 227° F. (108° C.) sample B reaches its optimum cure in about 60 minutes, while double the curing time

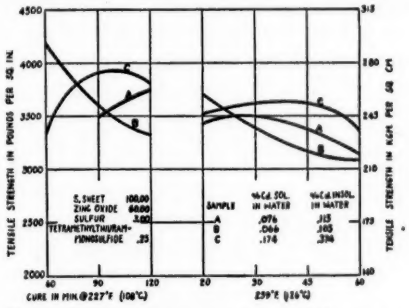

FIGURE 25. DATA ON THREE EXPERIMENTAL ZINC OXIDES

is required for sample A. Although sample A contains slightly more cadmium, it is not sufficient to account for the great difference in curing characteristics.

It is quite possible that the cadmium compounds present in these samples are not identical. Since their identity is not assured, several combinations are possible and it may be assumed that the insoluble cadmium in sample A is composed of cadmium oxide or a combination of oxide and hydroxide which accounts for the very slow curing properties. The cadmium compounds present in sample B may be different, and could be either the sulfide or carbonate, or a combination of the two.

Sample C contains appreciably more soluble and insoluble cadmium, but its curing properties range between those of A and B. Evidently, the cadmium compounds present in this sample are not the same as those in A and B, and their identity is a matter of conjecture.

The information used in the above discussion illustrates the necessity of knowing the exact form of the cadmium

present in a commercial zinc oxide in order to predict the effect when used with tetramethylthiouram monosulfide. The same is also true for each accelerator used in this work, as similar comparisons are possible with all of them.

Cadmium compounds have limited uses in the rubber industry at present; however, some interesting possibilities may be developed by further investigation.

Acknowledgment

The splendid assistance of Warren F. Mills in preparing the data for this paper and his helpful suggestions are gratefully acknowledged.

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Heat-Resisting Inner Tube Stocks

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To develop heat-resisting inner tube stocks, a method of testing, called air-bomb aging, has been devised. Tests showed that low sulfur, 1 to 1.25 per cent, high acceleration, 2 per cent or more based on the rubber content, relatively high percentages of antioxidant, and relatively high volume loading, 20 to 25 per cent based on the rubber content, were necessary to obtain a stock which would meet the requirements imposed by the air-bomb aging test.

RUBBER chemists and compounders have for a good many years realized that inner tubes should be compounded to withstand the high temperatures frequently developed in service. This is especially true of tubes for bus and truck tires. Several authorities have claimed that under extreme conditions tubes may reach temperatures as high as 250° or even 260° F. (121° or 126° C.). These temperatures are rather high and are undoubtedly seldom reached in actual practice, but it is probable that in ordinary service, temperatures up to 180° or even 200° F. (82° or 87° C.) are reached for short periods of time.

The earlier methods of compounding inner tube stocks against deterioration by heat will be mentioned here, but only briefly discussed. High percentages of zinc oxide compared to the rubber content were employed, and such stocks withstood deterioration due to heat quite satisfactorily when relatively low sulfur ratios, such as from 2.25 to 2.00 per cent, were used. It was known from aging and service tests that reclaimed or off-grade rubber could not be satisfactorily used. The stocks were purposely overcured. Quite high percentages of antimony pentasulfide were successfully employed.

However, zinc oxide and antimony pentasulfide are too expensive to be used today in the high percentages necessary, when compared to the other available fillers. The use of two accelerators of different types in the same stock frequently improved markedly the resistance to deterioration in service. A stock cured with a guanidine accelerator alone gave a brittle stock in service, possessing but little resistance to tear, and when a tube so compounded was punctured, a tear of from 6 to 12 inches (15.2 to 30.4 cm.) or more very often resulted. When used alone, an aldehyde-amine accelerator gave a stock which in service softened and increased in size and often failed because of pinching at the bead or folding back over itself. A combination of a guanidine and an aldehyde-amine accelerator was successfully used, and such a stock overcame the difficulties resulting from the use of either accelerator when employed alone. The use of an antioxidant materially lengthened the period of service of bus and truck inner tubes. The practice of curing on circular mandrels and later of curing in a watch-case heater also further improved these tubes.

During the past 5 years or more the tendency has been toward the use of smaller diameter and wider cross-section tires. Braking efficiency has been increased, non-skid tendencies have been improved, and the tires of today give two to three times the mileage in service that the tires of former years gave. Tread stocks of today are much stiffer or harder. These changes have resulted in an increase in the quantity of heat generated in the tire which is transmitted to the inner tube, and the chemist and compounder are back where they were a few years ago. Consequently, the inner tubes in bus and truck tires too frequently are not giving the service the manufacturer or user would like them to give.

Test for Heat-Resisting Qualities

The oxygen-bomb and Geer oven aging tests do not give the information necessary to compare inner tube stocks of this kind in the manner desired. Therefore, to enable the compounder to investigate the heat-resisting qualities of a stock, a special procedure was required. The writer does not claim to be the originator of this testing method. In the method to be described, an air bomb similar to that used in oxygen-bomb testing is used. The stocks to be tested are milled and cured in the regular way, and dumbbell strips are prepared from the cured stock as for use in the Scott testing machine. Two strips from each stock are placed in a rack, and in the procedure followed in the experiments described, were elongated 50 per cent. This rack is placed inside the bomb which is then closed and placed in a laboratory Williams open steam heater which is jacketed. As determined by experiment, the temperature inside the bomb is about 10° F. (5.5° C.) less than the temperature inside the heater, and therefore a 10° F. higher temperature is employed in the

heater. There is a lag of about 20 to 30 minutes between the times the heater and the bomb get up to temperature. The air pressure inside the bomb increases as the temperature increases; therefore, in practice air is not put into the bomb until the temperature has been brought up to the required point. Then air is forced into the bomb and retained by closing a valve located between the air supply and the pressure gage. A recording thermometer records the temperature in the heater, and a pressure gage records the air pressure during the test. Standard practice in this laboratory is to employ 100 pounds air pressure at 250° F. (121° C.), over a period of from 8 to 18 hours with the stock under an elongation of 50 per cent.

Preliminary tests before adopting these standards showed that the 8-hour age tests eliminated a great many stocks, the 12-hour age tests still more, and that those stocks which after 18 hours' aging had lost only 25 to 40 per cent of their original tensile strength would be quite satisfactory for longer aging periods. A few tests were made with higher and lower air pressures than 100 pounds, showing that as the air pressure was increased the period of the test could be shortened, but the difference in time between 75 and 150 pounds air pressure was only 2 to 3 hours. Tests before adopting 250° F. (121° C.) as standard temperature showed that increasing the temperature quite rapidly shortened the time required for deterioration of the stocks. This temperature, 250° F. (121° C.), was chosen as standard because it was sufficiently high to eliminate moisture, permitted the use of steam as the means of obtaining temperature, and was high enough to be controlled during a test.

Oxygen-Bomb and Air-Bomb Tests

The scope of this paper is to review laboratory tests, covering more than a year's time, carried out to develop heat-resisting inner tube stocks. As is true of all laboratory tests, their value lies in their interpretation of service results. Unfortunately information is not available concerning service tests on any of the stocks given in this paper, and the only reason for believing that the results reported are comparable to service tests is that they compared favorably with those obtained from commercial heat-resisting inner tubes of proven merit.

Table I. Effects of Reducing Sulfur

Base Stock		Stock No.	Sulfur
			%
Smoked sheets	100	...	...
P-33 Black	40	B-5-A	2.00
Zinc oxide	5	B-5-B	1.75
Stearic acid	1	B-5-C	1.50
Antioxidant	1	B-5-D	1.25
Ureka C	1.60	B-5-E	1.00
D. P. G.	0.40	...	..

Cures: 6, 9, 12, 15 min. at 60 lb. steam pressure, 307° F. (153° C.). Air-bomb aging, 18 hr.; 50% elongation; 100 lb. air pressure at 250° F. (121° C.). Plastometer tests: 0, 45, 60, 90 min. at 100° C.

In order to obtain a comparison between the oxygen-bomb and air-bomb tests, a tread stock of high quality containing an antioxidant was aged 48 hours at 70° C. under 300 pounds oxygen pressure in the oxygen bomb. Tests showed that this stock lost approximately 30 per cent of its original tensile strength after aging, whereas the same stock, when subjected to the conditions described in the air bomb for 18 hours, lost 90 per cent of its original tensile strength. Likewise, a heat-resisting inner tube stock lost 25 per cent in tensile strength in the oxygen bomb and only 30 per cent in the air bomb. Also a good truck tube stock containing an antioxidant was aged in the oxygen bomb under the above conditions, and after 48 hours' aging lost 25 per cent of its original tensile strength, but when subjected to the conditions in air-bomb aging, was so deteriorated after 18 hours that it could not be tested. Accordingly, the air bomb seems a reliable test to follow in comparing heat-resisting inner tube stocks and,

TABLE II. PHYSICAL TESTS BEFORE AGING

CURE	STOCK NO.	SULFUR	MODULUS AT 300%	MODULUS AT 500%	MODULUS AT 700%	TENSILE AT BREAK	ULT. ELONG
Min./lb.		%				*Lb.*	
6/60	B-5-A	2.00	516	1685	3890	4290	730
	B-5-B	1.75	485	1625	3795	4260	735
	B-5-C	1.50	456	1560	3680	4180	740
	B-5-D	1.25	418	1443	3490	4210	750
	B-5-E	1.00	391	1435	3480	4165	750
9/60	B-5-A	2.00	557	1945	..	4235	695
	B-5-B	1.75	535	1870	..	4135	690
	B-5-C	1.50	500	1805	4000	4275	720
	B-5-D	1.25	476	1710	3980	4110	725
	B-5-E	1.00	461	1650	3860	4280	730
12/60	B-5-A	2.00	598	2015	..	4205	690
	B-5-B	1.75	575	1940	4210	4210	700
	B-5-C	1.50	520	1880	4165	4200	705
	B-5-D	1.25	486	1785	4015	4305	715
	B-5-E	1.00	463	1740	3965	4200	715
15/60	B-5-A	2.00	635	2065	..	4315	690
	B-5-B	1.75	600	1960	..	4290	695
	B-5-C	1.50	580	1890	4350	4350	700
	B-5-D	1.25	535	1825	4095	4365	715
	B-5-E	1.00	513	1805	4075	4375	720

including as it does a combination of pressure, elongation, and temperature, closely approximates the conditions to which the tube is subjected in service. The test, of course, is exaggerated, but exaggerated as nearly all laboratory tests, to give a quick method of comparison of stocks. The author believes he has reliable information showing that stocks which stand up in the air-bomb tests also stand up in service.

The laboratory study of the problem of developing a heat-resisting stock started with a study of various accelerators. Early tests were carried out by employing 2 per cent sulfur on the rubber content and by varying the amounts of the various accelerators used. Excellent results were obtained until the stocks were subjected to the air-bomb test. Some accelerators were slightly better than others, but all failed. All the known antioxidants were included in the test, but none was capable of producing a stock which aged satisfactorily in the air bomb. On varying the sulfur ratio, when

the sulfur ratio was as low as 1.25 to 1 per cent on the rubber content, greatly improved results were obtained, as shown in Table I. The physical tests obtained on the stocks in Table I before aging are given in Table II, after aging in Table III.

TABLE III. PHYSICAL TESTS AFTER AIR-BOMB AGING FOR 18 HOURS

CURE	STOCK NO.	SULFUR	MODULUS AT 300%	MODULUS AT 500%	MODULUS AT 700%	TENSILE AT BREAK	ULT. ELONG.
Min./lb.		%				*Lb.*	
6/60	B-5-A	2.00	918	2545	..	2575	505
	B-5-B	1.75	875	2470	..	2640	520
	B-5-C	1.50	830	2380	..	2840	545
	B-5-D	1.25	790	2305	..	3020	590
	B-5-E	1.00	750	2260	..	3125	605
9/60	B-5-A	2.00	823	2120	..	2120	500
	B-5-B	1.75	790	2100	..	2275	510
	B-5-C	1.50	770	2150	..	2565	520
	B-5-D	1.25	723	2200	..	2670	580
	B-5-E	1.00	685	2205	..	3000	610
12/60	B-5-A	2.00	799	1975	..	1975	500
	B-5-B	1.75	774	1960	..	2105	510
	B-5-C	1.50	750	2045	..	2395	520
	B-5-D	1.25	715	2015	..	2670	560
	B-5-E	1.00	690	2100	..	2955	600
15/60	B-5-A	2.00	775	..	..	1725	465
	B-5-B	1.75	755	..	..	1930	490
	B-5-C	1.50	740	2000	..	2175	510
	B-5-D	1.25	715	1960	..	2490	535
	B-5-E	1.00	699	1910	..	2625	570

TABLE IV. LOSSES IN TENSILE STRENGTH DUE TO AIR-BOMB AGING

STOCK NO.	SULFUR	6/60 LB.	9/60 LB.	12/60 LB.	15/60 LB.
	%	%	%	%	%
B-5-A	2.00	40	50	53	60
B-5-B	1.75	38	45	50	55
B-5-C	1.50	32	40	43	50
B-5-D	1.25	28	35	38	43
B-5-E	1.00	25	30	32	40

TABLE V. WILLIAMS PLASTOMETER TESTS

STOCK NO.	SULFUR	NO PRE-HEATING	45/100° C.	60/100° C.	90/100° C.
	%				
B-5-A	2.00	152	197	248	540
B-5-B	1.75	153	179	241	510
B-5-C	1.50	152	179	197	439
B-5-D	1.25	149	160	187	323
B-5-E	1.00	147	148	160	191

These stocks show that as the sulfur ratio is reduced from 2 to 1 per cent the stocks age better in the air bomb (Table IV). The effect of too much cure at high temperatures is also shown. The plastometer tests, given in Table V, also show that 1 per cent sulfur stock would handle more easily in the factory than the 2 per cent sulfur stock. As will be shown later, 2 per cent antioxidant gives even better results in the 1 per cent sulfur stock, and also helps to overcome the effect of overcure (or long cure).

TESTING PROCEDURE

The following procedure was carried out in making all laboratory tests: The stocks were milled on cool mills at

about 70° F. (21.1° C.). The cures were carried out in the regular way using two platen presses and curing a strip 4.5 by 6.5 inches (11.4 by 16.5 cm.). The method of air-bomb aging has already been described. The plastometer tests were made on a Williams plastometer. The time designated is the time the stocks were kept in an electric oven at the designated temperature, after which the pellets were allowed to come to room temperature (about 30 minutes to 1 hour being allowed for this cooling), and then heated again for 10 minutes at 70° C. before putting in the plastometer which is kept in a separate oven at 70° C. The readings recorded were taken after 3 minutes in the Williams plastometer with the weight pressing down on the pellets. No recovery figures were taken. A metal tray is used in the plastometer to be sure the pellets are in the center of the platens. The lowest reading possible is therefore 141.

The method of taking permanent set figures is to remove the test strips from the rack after aging in the air bomb, and allow them to remain in the constant-temperature testing room (70° F.) for 30 minutes, then to measure the distance between the bench marks which were put on the strips before putting into the rack, elongated 50 per cent, and aged. For example, a figure of 30 per cent permanent set means that after aging the original bench marks 1 inch (2.54 cm.) apart are now 1.3 inches (3.3 cm.).

The per cent loss in tensile strength due to air-bomb aging is arrived at by subtracting the tensile strength after aging from the original tensile strength and dividing the difference by the original.

The per cent loss in tensile strength is influenced by the original and is believed to be a criterion for comparing the heat-resisting qualities of a stock. Before aging, the four stocks designated in the tables are almost identical in tensile strength. In none does the modulus drop off showing serious overcure, and yet after being subjected to the air-bomb test marked differences in tensile strengths are evident. These differences were caused by the air-bomb aging, and since a commercial tube of proven quality, tested in an identical manner, lost only approximately 35 per cent of its original tensile strength after 18 hours' aging, it is believed that percentage loss in tensile strength due to air-bomb aging is a criterion useful in comparing heat-resisting inner tube stocks.

No tests except those carried out by hand were made to show the resistance of the stocks to tear. None of the stocks equaled a quality tread stock nor a quality gum inner tube stock in resistance to tear. It is believed that resistance to tear is a factor of particle size and quantity of the filler used, together with the degree of cure and dispersion of filler. The comparison of modulus is considered as showing quite accurately the resistance to tear when similar stocks are thus compared.

Flexing tests were made on a number of the stocks tested, but are not given here since their presentation of necessity requires a discussion of machines used and theories involved which would furnish sufficient data for a paper of considerable size.

Sulfur ratios lower than 1 per cent on the rubber content were investigated to a limited extent only. It was found that with less than 1 per cent sulfur, the modulus and tensile figures dropped quite rapidly. The author's theory in this connection is that a satisfactory stock should have a tensile strength before aging of over 3000 pounds. No advantage was found in stocks containing less than 1 per cent sulfur as regards percentage loss in tensile, resistance to tear, or flexing qualities.

Ureka C, which is used as accelerator in some of these stocks, is a mercaptobenzothiazole reaction product which, when used alone in stocks of this type, is not a powerful accelerator but, when used in conjunction with a guanidine, is a powerful accelerator possessing unusual handling qualities. Guantal is a guanidine containing material which, when employed in conjunction with Ureka C, further improves its handling qualities and enables the use of larger quantities of accelerator with corresponding increased acceleration.

Accelerators, Antioxidants, and Fillers

In view of the good results obtained with 1.25 to 1 per cent sulfur, a study of various accelerators was made. The aldehyde-amine group gave excellent results before the stocks were aged in the air bomb, but in this test they would not hold up no matter what antioxidant was used. By the expression "hold up" is meant that the tensile strength after air-bomb aging would drop as much as 50 per cent. Although such a stock is good, is satisfactory for passenger-car inner tubes, and would give fair service in a bus or truck tube, even better results were desired. The guanidine accelerated stocks likewise dropped 50 per cent or more in tensile strength after air-bomb aging. A combination of an aldehyde-amine and a guanidine was a little better, but still not equal to the desired results. Most all of the other accelerators tested had one or both of the following objections:

1. Some accelerators with the low sulfur ratios employed failed to give tensile figures in the unaged stock of 2000 pounds or higher.
2. Some accelerators gave excellent modulus and tensile figures both before and after air-bomb aging, but the plastometer test showed they would be difficult to handle (scorchy).

The possibility of using a retarder was investigated, but there was not available a commercial retarder of sufficient activity in the stocks tested to permit the use of the larger amount of accelerator necessary.

The only accelerator which seemed to meet all the specifications was Ureka C. Captax gave satisfactory unaged and

aged results, but when employed in the amounts necessary to obtain favorable unaged tensile and modulus figures, the plastometer tests showed that the stocks would be somewhat scorchy, a factor which might cause difficulty in handling in the factory.

The importance of the antioxidant and amounts necessary were next investigated. Most of the antioxidants available on the market were tested, some proving better than others. It was shown that the customary 1 per cent on the rubber content was not enough for this stock or, stated differently, 1.5 and 2 per cent antioxidant showed enough increase in tensile after air-bomb aging to warrant the use of these quantities.

TABLE VI. COMPARISON OF BLANC FIXE AND P33 BLACK

BASE STOCK		STOCK NO.	MATERIAL ADDED	AMT.
				%
Smoked sheets	100	....	.....	..
Zinc oxide	5	B-17-A	P33 Black	40
Stearic acid	1	B-17-B	Blanc fixe	30
Ureka C	1.6	B-17-C	Blanc fixe	40
D. P. G.	0.4	B-17-D	Blanc fixe	88
Antioxidant	1	....	.....	..
Sulfur	1	....	.....	..

Cures: 6, 9, 12, 15 min. at 60 lb. steam pressure, 307° F. (153° C.). Air-bomb aging, 18 hr.; 50% elongation; 100 lb. air pressure at 250° F. (121° C.).

TABLE VII. PHYSICAL TESTS BEFORE AGING

CURE	STOCK NO.	FILLER	AMT.	MODULUS AT 300%	MODULUS AT 500%	MODULUS AT 700%	TENSILE AT BREAK	ULT. ELONG.
Min./lb.			%				*Lb.*	
6/60	B-17-A	P33 Black	40	391	1435	3480	4170	750
	B-17-B	Blanc fixe	30	275	882	2650	2850	720
	B-17-C	Blanc fixe	40	328	1115	3140	3140	700
	B-17-D	Blanc fixe	88	332	1185	3360	3485	715
9/60	B-17-A	P33 Black	40	463	1675	3840	4310	745
	B-17-B	Blanc fixe	30	310	1010	2750	2985	715
	B-17-C	Blanc fixe	40	332	1228	3340	3340	700
	B-17-D	Blanc fixe	88	346	1305	3475	3505	705
12/60	B-17-A	P33 Black	40	473	1695	3950	4305	725
	B-17-B	Blanc fixe	30	301	943	2565	2565	700
	B-17-C	Blanc fixe	40	374	1315	..	3360	680
	B-17-D	Blanc fixe	88	378	1340	..	3450	660
15/60	B-17-A	P33 Black	40	513	1790	4050	4325	710
	B-17-B	Blanc fixe	30	308	955	2570	2570	700
	B-17-C	Blanc fixe	40	379	1338	..	3320	670
	B-17-D	Blanc fixe	88	384	1390	..	3380	655

Early tests were carried out with P33 Black as filler, and it gave excellent results. However, the stock is black, and it was thought desirable to investigate other fillers which would give a stock capable of being colored (red, blue, green, etc.). Zinc oxide, blanc fixe, barytes, and precipitated whiting were found to be very good, but clay did not test favorably. Such stocks did not give as high modulus or tensile figures as P33 Black in the unaged tests, but the per cent loss due to air-bomb aging was equal to P33 Black and the stocks were neutral enough in color to be colored red, green, blue, or any other color desired. Table VI gives a comparison of blanc fixe and P33 Black and also the value of different loadings,

Table VII gives the physical tests on the stocks used before aging, and Table VIII the tests after aging. Table IX gives the losses due to the aging.

TABLE VIII. PHYSICAL TESTS AFTER AIR-BOMB AGING FOR 18 HOURS

Cure	Stock No.	Filler	Amt.	Modulus at 300%	Modulus at 500%	Modulus at 700%	Tensile at Break	Ult. Elong.
Min./lb.			%				*Lb.*	
6/60	B-17-A	P33 Black	40	755	2280	..	3120	605
	B-17-B	Blanc fixe	30	309	935	..	2050	660
	B-17-C	Blanc fixe	40	339	1075	..	2230	665
	B-17-D	Blanc fixe	88	342	1230	..	2675	670
9/60	B-17-A	P33 Black	40	625	2225	..	3100	615
	B-17-B	Blanc fixe	30	282	945	..	2120	660
	B-17-C	Blanc fixe	40	291	1055	..	2120	650
	B-17-D	Blanc fixe	88	355	1420	..	2500	670
12/60	B-17-A	P33 Black	40	645	2155	..	3065	600
	B-17-B	Blanc fixe	30	285	948	..	1640	640
	B-17-C	Blanc fixe	40	298	1063	..	2085	660
	B-17-D	Blanc fixe	88	357	1428	..	2500	670
15/60	B-17-A	P33 Black	40	653	2088	..	2775	580
	B-17-B	Blanc fixe	30	284	933	..	1490	625
	B-17-C	Blanc fixe	40	296	1054	..	1990	640
	B-17-D	Blanc fixe	88	344	1515	..	2215	630

TABLE IX. LOSSES DUE TO 18-HOUR AIR-BOMB AGING

Stock No.	6/60 lb.	9/60 lb.	12/60 lb.	15/60 lb.
	%	%	%	%
B-17-A	25	28	29	36
B-17-B	28	29	36	42
B-17-C	29	36.5	38	40
B-17-D	23	28.5	27.5	34.5

It appeared, as has been stated above, that the most desirable results were obtained from a stock containing a low ratio of sulfur and a high ratio of antioxidant. Consequently, stocks were run incorporating previous findings, and the results obtained on four typical ones are shown in Table X.

TABLE X. RESULTS OBTAINED ON TYPICAL STOCKS

B-73	A	B	C	D
Smoked sheets	100	100	100	100
P-33 Black	40	40	40	40
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Sulfur	.	1	1	1
Tuads	2	.	.	.
Agerite resin	1	.	1	.
Neozone D	1	.	1	.
Ureka C	.	2	.	1.6
Guantal	.	0.8	.	.
Flectol A	.	2.0	.	2.0
Captax	.	.	2	.
D. P. G.	.	.	.	0.4

Cures: 6, 9, 12, 15 min. at 50 lb. steam pressure, 298° F. (148° C.). Air-bomb aging, 18 hrs. at 250° F. (121° C.), 100 lb. air pressure; 50% elongation. Plastometer tests: 120, 180, 240, 300 min. at 180° F

Table XI gives the physical tests obtained on these stocks before aging, Table XII gives them after aging, Table XIII shows the loss in tensile strength after aging, Table XIV the permanent set figures, and Table XV the plastometer tests.

Table XI. Physical Tests before Aging

Cure	Stock No.	Modulus at 300%	Modulus at 500%	Modulus at 700%	Tensile at Break	Ult. Elong.
Min./lb.					*Lb.*	
6/50	B-73-A	548	1673	..	3820	690
	B-73-B	510	1575	3940	4260	710
	B-73-C	486	1365	3460	3540	705
	B-73-D	490	1490	3225	3425	710
9/50	B-73-A	571	1745	..	3880	680
	B-73-B	543	1633	4410	4410	700
	B-73-C	492	1405	..	3620	695
	B-73-D	511	1555	..	3860	690
12/50	B-73-A	565	1770	..	3980	695
	B-73-B	560	1750	..	4405	695
	B-73-C	495	1410	..	3705	690
	B-73-D	534	1623	..	3960	690
15/50	B-73-A	591	1815	..	3915	690
	B-73-B	593	1843	..	4500	695
	B-73-C	496	1415	..	3760	685
	B-73-D	542	1660	..	4015	685

Table XII. Physical Tests after Air-Bomb Aging for 18 Hours

Cure	Stock No.	Modulus at 300%	Modulus at 500%	Modulus at 700%	Tensile at Break	Ult. Elong.
Min./lb.					*Lb.*	
6/50	B-73-A	691	1780	..	2680	620
	B-73-B	715	1965	..	3210	650
	B-73-C	702	1810	..	2360	640
	B-73-D	684	1610	..	2840	660
9/50	B-73-A	623	1823	..	2540	615
	B-73-B	720	1970	..	3090	640
	B-73-C	690	1765	..	2410	645
	B-73-D	698	1740	..	2875	650
12/50	B-73-A	600	1790	..	2480	605
	B-73-B	720	1960	..	3080	630
	B-73-C	680	1750	..	2400	650
	B-73-D	700	1768	..	2870	640
15/50	B-73-A	537	1638	..	2395	600
	B-73-B	715	1980	..	2970	620
	B-73-C	658	1740	..	2375	650
	B-73-D	716	1810	..	2750	630

Table XIII. Losses in Tensile Strength Due to Air-Bomb Aging

Stock No.	6/50 lb.	9/50 lb.	12/50 lb.	15/50 lb.
	%	%	%	%
B-73-A	30	34.6	40	40
B-73-B	25	30.0	30	34
B-73-C	31.6	33.0	35	37
B-73-D	20.6	25.5	27.5	31.5

Table XIV. Permanent Set Figures after Air-Bomb Aging

Stock No.	6/50 lb.	9/50 lb.	12/50 lb.	15/50 lb.
	%	%	%	%
B-73-A	30	30	30	30
B-73-B	35	30	27.5	25
B-73-C	35	35	40	40
B-73-D	35	32.5	30	30

Table XV. Williams Plastometer Tests

Stock No.	120/180° F.	180/180° F.	240/180°F.	300/180° F.
B-73-A	141	141	141	141
B-73-B	141	152	162	197
B-73-C	191	290	350	514
B-73-D	141	141	157	161

Conclusions

A large number of laboratory tests were carried out which showed that to resist deterioration due to heat in an inner tube stock successfully, the following points should be observed:

1. Sulfur ratios should be very low. One per cent on the rubber content is sufficient for most stocks; some will require 1.2 per cent. This is true provided no sulfur-producing material is present.
2. When P33 Black or a similar soft black is used, 20 to 25 volumes are necessary. In the case of zinc oxide, blanc fixe, barytes, and the like, lower volumes will be necessary to obtain satisfactory resistance to tear.
3. The stocks should not be markedly overcured, especially if the cure is carried out at 50 pounds steam pressure (298° F.) or above. This is the opposite of former practice with stocks of higher sulfur ratio.
4. The accelerator chosen must be strong enough to combine practically all of the sulfur present, and yet should not be too scorchy to handle safely in the plant.
5. Tests showed that the use of 2 per cent of a good antioxidant was justified. One per cent gave good results, but especially when agings longer than 18 hours were carried out the stocks containing 2 per cent were markedly superior.
6. Zinc oxide, blanc fixe, barytes, or precipitated whiting can be successfully employed in stocks of this type. The modulus and tensile figures are lower than when P33 Black is used, but the losses in tensile strength due to air-bomb aging are comparable to P33 Black, and these fillers would permit the manufacture of colored tubes such as red, green, and yellow.
7. Heat-resisting inner tube stocks of this type compared to the ordinary tread, carcass, and tube stocks will necessarily be more scorchy, and care must be taken to cool the stocks properly in processing through the factory.

The possibility of the migration of sulfur from the carcass stocks to the inner tube, or the migration of accelerator from the inner tube stock to the carcass stock must be taken into account. Today tire manufacturers are using as low as 2 per cent sulfur in the carcass stocks of bus and truck tires. These low sulfur ratios in the carcass stock tend to prevent the migration of sulfur. The usual Geer oven migration tests were carried out on stocks containing Ureka C as accelerator. The Geer oven was maintained at 93.3° C. (200° F.) for 14-day periods, and in no case did these tests show appreciable migration of sulfur or accelerator. Controls were run during the migration tests and alone.

Presented before the Meeting of the Division of Rubber Chemistry of the American Chemical Society, Detroit, Mich., February 25 and 26, 1932.

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Solubility of Organic Compounds in Rubber

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A method for determining the solubility of organic compounds in rubber has been developed. Apparatus consisting of a constant-temperature oven designed to permit microscopic observation of the material in the oven has been constructed to facilitate the use of this method. Solubility data have been obtained on a number of organic compounds now commercially available to the rubber trade. An application of the solubility data to molecular weight determination has been made. Discussion of other uses for the solubility data is included.

SINCE there is available considerable evidence that vulcanization and oxidation take place homogeneously in the rubber phase, the solubility of accelerators, antioxidants, scorch retarders, and softeners in rubber is of importance. While the activity of various organic materials used in compounding is primarily dependent upon their chemical structure, concentration must be considered; and, in the cases of the less soluble materials, solubility becomes the limiting factor. Similarly, the well-known phenomena of blooming and bleeding of organic compounds in rubber are directly due to solubility.

Because a knowledge of the solubility of organic compounding materials in rubber is important, not only as an explanation of well-known phenomena but also as an aid to future

developments, extension and amplification of the rather meager data now available seemed imperative.

Previous Work

Commercial-grade rubber is a heterogeneous system containing as impurities both proteins and fatty acids to the extent of 2 to 3 per cent of the total weight. Pure rubber is generally regarded as highly polymerized isoprene, an unsaturated hydrocarbon having the empirical formula C_5H_8. At room temperature, x-ray data (*3*) show that rubber in the unstressed state is entirely amorphous, having identically the same diffraction pattern as a liquid, but, when extended, definite indications of crystallinity appear. Acken, Singer, and Davey (*1*) have recently published x-ray data to indicate that rubber exists as a two-phase system—a gel consisting of the high and low polymers of isoprene which are mutually soluble at room temperature in the unstressed state, but which, when subjected to stress, are rendered somewhat less mutually soluble, thus giving rise to the typical fiber x-ray diagram. Either removal of stress or heating destroys the diffraction pattern.

The solubility of a variety of gases in rubber has been determined by Venable and Fuwa (*9*). The general solubility rules for gases in solids and liquids were observed, the solubility varying as the pressure and inversely as the temperature; the higher the critical temperature, the more soluble is the gas. Williams and Neal (*10*) made a very careful survey of the solubility of oxygen in rubber and observed that at slightly elevated temperatures there was a reaction between the oxygen and rubber whereby the apparent solubility was changed.

Bruni (*2*) showed that organic compounds formed true solutions with rubber by measuring the depression of the freezing point of azobenzene, naphthalene, and *p*-toluidine, produced by the addition of varying amounts of deresinated rubber. Because of the importance of the subject, the solubility of sulfur in rubber has been studied by two sets of investigators. Green and Venable (*6*) determined the solubility of sulfur in vulcanized rubber by heating it packed in powdered sulfur until solubility equilibrium was attained, the amount of free sulfur being obtained by analysis. Kelly and Ayres (*8*) determined the solubility of sulfur in rubber by carrying out distribution experiments between butyl alcohol and rubber with a wide range of coefficients of vulcanization. The results, while not in exceedingly good agreement with those of Green and Venable (*6*), are of the same order, and are undoubtedly more accurate. Endres (*4*, *5*) in his work on the crystallization of sulfur in rubber has shown that the crystalline form and habit varies widely with the previous history of the mixture.

Purpose of Investigation

Because there are virtually no data available on the solubility of organic compounds in rubber beyond that inferred in the

words "blooming" and "nonblooming" as applied to various compounded stocks, it has been the purpose of this investigation to devise an easy and rapid method of measuring the solubility of solids in rubber, and to accumulate sufficient data to aid in the explanation of a variety of phenomena. It has been hoped that, with the accumulation of data, certain properties of compounds will become readily predictable, knowledge which should be of aid in obtaining compounds of greater usefulness to the rubber chemist.

The work thus far has been confined to systems of rubber and one other component only in order to establish a basis of knowledge for more extensive investigations of the systems of three and more components of practical interest.

A method has been devised and apparatus constructed

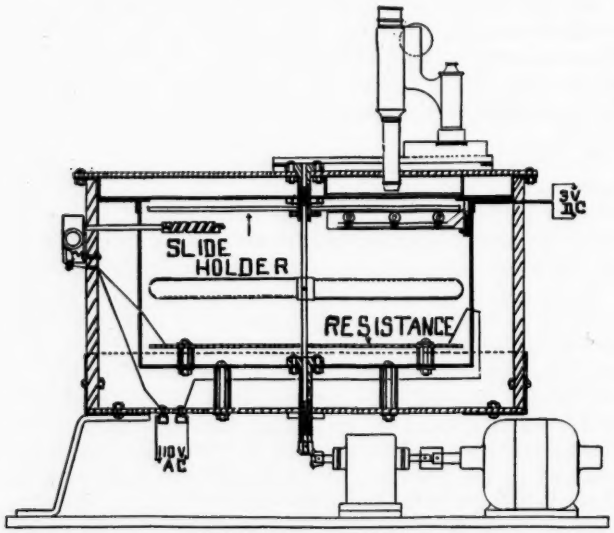

FIGURE 1. DIAGRAM OF APPARATUS

which has made solubility investigations both rapid and easy. This apparatus is shown in Figures 1 and 2. Using this method the solubility in uncured rubber of a number of organic compounding agents has been determined from room temperature to vulcanization temperatures. The results on materials now on the market are shown graphically in Figures 3 and 4. Figure 3 shows the solubility of a few of the more soluble compounds, while Figure 4 indicates the results on some less soluble.

APPARATUS

The methods of Green and Venable (*6*) and Kelly and Ayres (*8*), while suitable for solubility measurements of sulfur in rubber, are lengthy and involve a rather tedious analysis. However, methods of analysis for a great many of the com-

pounds used in the rubber industry are very sketchy or nonexistent, thus making their methods even more difficult. Preliminary observations with a microscope hot stage on the rate of approach to solubility equilibrium of materials soluble in rubber indicated that methods which utilize changes in heat content upon solution were definitely excluded, since 5 hours or longer are required for equilibrium at low temperatures. Such changes are not measured readily when extended over long periods of time. Similarly, serious use of the microscope hot stage was excluded, since it is virtually impossible to construct a hot stage which will ensure uniform heating and maintain constant temperature.

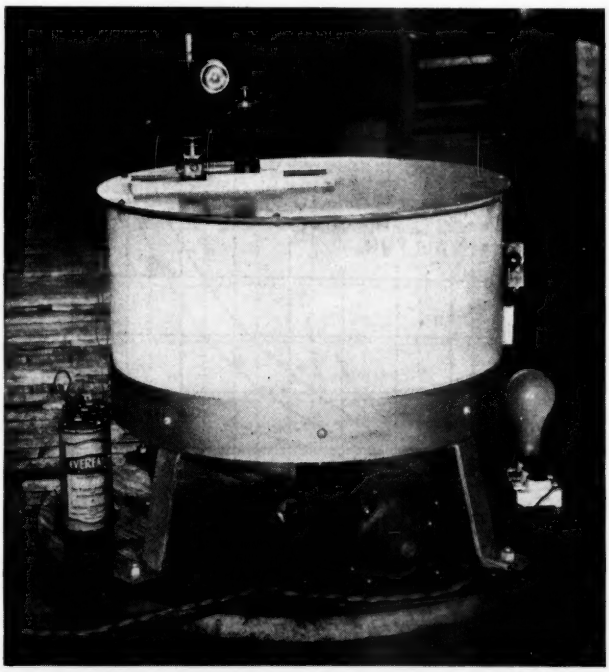

FIGURE 2. PHOTOGRAPH OF APPARATUS

An apparatus which would permit microscopic observation of specimens over long periods of time at constant temperature up to vulcanization temperatures was designed and constructed. It is shown in Figures 1 and 2.

The apparatus is essentially a double-wall cylindrical oven equipped with a circular glass-plate slide holder which is rotated at 12 r. p. m. by an electric motor through a set of reducing gears. The outer shell is Transite pipe, 20 inches (50.8 cm.) inside diameter and 11 inches (27.9 cm.) high. The inner shell is of welded sheet iron 16 inches (40.6 cm.) in diameter, 8 inches (20.3 cm.) high, leaving a 2-inch (5-cm.) wall space which is packed with Sil-O-Cel. The top cover also is made of Transite

and welded sheet iron with 1 inch (2.5 cm.) of Sil-O-Cel insulation.

A B & S No. 26 nichrome wire resistance about 25 feet (4.9 meters) long, drawing 1.6 amp. at 110 volts a. c., mounted on a Transite base, is used for the heating element. Temperature control is obtained by use of a bimetallic thermoregulator fixed just below the slide holder. Air circulation is ensured by an agitator fixed to the plate holder shaft.

The microscope is mounted on a carriage sliding on a double track, the specimens being viewed through a window in the top cover. The microscope, which has a slight extension to permit focusing on the specimen, uses a 32-mm. objective and a 10X eyepiece. Three flash-light bulbs fixed below the slide holder, backed by a stainless steel reflector, comprise the illuminating system.

With this apparatus, twenty to thirty specimens in a single run may be examined at any temperature from 25–160° C., for any length of time.

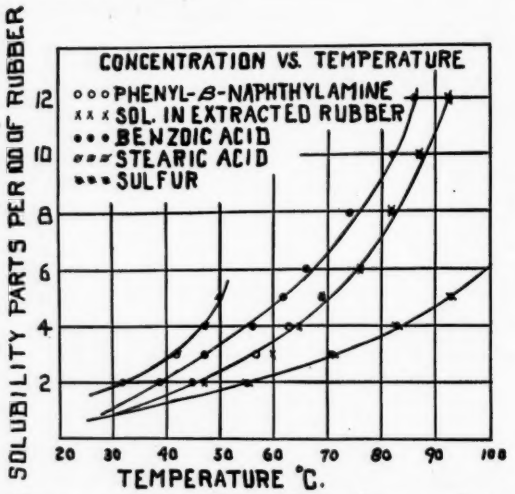

FIGURE 3. SOLUBILITY OF MORE SOLUBLE COMPOUNDS

PROCEDURE

The procedure used in solubility determinations is very simple. The compound to be studied is milled into clean selected sheets of pale crepe on a laboratory mill to a given concentration. It has been found easiest and most accurate to prepare a master batch and dilute to the concentration desired. When the solubility characteristics are unknown, it is advisable to make a preliminary survey at a low, intermediate, and high concentration to aid in selecting a series of concentrations which will cover a large temperature range.

Thin sheets of the stock are placed between microscope slides and fastened to the plate-glass slide holder with gummed labels. Mounted with the slides are several calibrated thermometers to determine accurately the temperature of the slides.

With the oven assembled, the slides are carefully examined, and the state of the crystals or crystal fragments noted on each slide. This temperature is raised to about 40° C. and left at that point until no further changes in the state of solution are noted. By raising the temperature a few degrees at each step and noting the condition of the slides, an accurate idea of the temperature at which a given concentration is just completely soluble may be obtained. With this information a second run is made in which the temperature is kept 1–2° C. below the estimated temperature for complete solution for each concentration, and the behavior noted. If solution is complete a degree or two lower than first estimated, a third run may be made to confirm the results. The solubility in most cases may be established with an error of ±0.1 per cent or less.

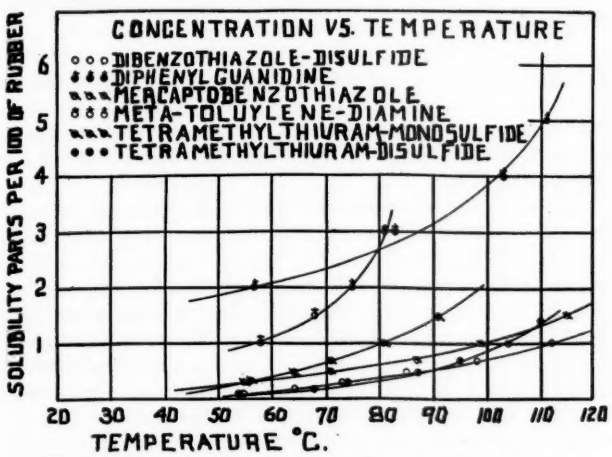

FIGURE 4. SOLUBILITY OF LESS SOLUBLE COMPOUNDS

While it is theoretically possible to determine the solubility of a substance by approaching the solubility equilibrium from the high temperature side, the phenomenon of supercooling is so general in rubber solutions (owing no doubt to the slow rate of migration of the soluble constituent through the rubber) that no instance has been found where credence could be attached to the results obtained in this way. Since there is no theoretical objection to the low-temperature approach, providing sufficient time is allowed for equilibrium to be attained, it has been used exclusively for solubility determination by this method.

DISCUSSION OF RESULTS

While a theoretical discussion of solubility is out of place in this paper, it is worthy of note that the general solubility rules for solids in liquids are applicable to rubber solutions, the higher the temperature the greater the solubility, and the lower the melting point of the solute the greater the

solubility. It is also observed that, in general, all compounds containing sulfur are very slightly soluble.

In this connection it is to be noted that only those compounds which have a relatively high solubility show any tendency to bloom. The compounds which tend to bloom are those which have a low solubility at room temperature and a high solubility at milling or vulcanization temperatures. This may undoubtedly be attributed to complete solution at the high temperature and the fact that, because of the absence of crystal fragments which serve as nuclei for recrystallization, a supersaturated condition results. In the absence of nuclei, crystallization shows preference for interfaces, particularly air-liquid or air-solid interfaces.

In support of these conclusions it has been observed that all of the compounds appearing in Figure 3 have a tendency to bloom. By this it is not meant that these compounds will bloom under any circumstances, but that certain stocks containing these compounds have been known to bloom, and that the bloom has been definitely identified as the substance in question. The compounds in Figure 4, however, have been classed as nonblooming, since no instance has been found in which they have been definitely identified in a bloom on the surface of a stock.

Reasoning from the assumption that blooming of compounds in rubber stocks is caused by a complete solution of the compound at a temperature above room temperature, a consequent disappearance of fragments serving as nuclei for recrystallization in the rubber, resulting in a supersaturated state upon recooling which is relieved by crystallization at the air-rubber interface, means can be devised for preventing bloom. The first expedient, and the one most commonly used, is to reduce the concentration of the component to the point at which it is completely soluble at room temperature. A second method is to add some substance which will either increase the solubility to the point where it is completely soluble at room temperature, serve as nuclei for recrystallization, or react with the excess to reduce the concentration or inhibit crystallization on the surface. Undoubtedly all of these methods are in use today, but a thorough investigation might readily extend their usefulness.

Another class of compounds is that which has been observed to undergo decomposition at temperatures well below ordinary vulcanization temperatures; thiocarbanilide is an excellent example. At temperatures over 60° C., the apparent solubility of thiocarbanilide changes continuously with time, indicating decomposition. The odor of phenyl mustard oil around a mill upon which a thiocarbanilide stock is being processed appears to support this conclusion.

Molecular Weight of Rubber

One of the theoretical results of Raoult's ideal solution law is that, if the logarithm of the mole fraction soluble at a given

temperature is plotted against the reciprocal of the absolute temperature, the resulting curve should be a straight line. Since the molecular weight of rubber is still a somewhat uncertain quantity, the mole fraction cannot be obtained, but, if a similar function (the logarithm of the weight per cent solubility) is plotted against the reciprocal of the absolute temperature as in Figure 5 the result is a straight line.

Using the equation for the solubility of solids in liquids as developed by Hildebrand (7), and supplying the heat of fusion from the International Critical Tables, it is possible to estimate the molecular weight of rubber. With the latent heat of fusion of sulfur (9.4 cal. per gram) and the data from the results on solubility in rubber, the molecular weight is calculated to be 22,200. Assuming the heat of fusion of benzoic acid as 19.2 cal. per gram, the molecular weight of rubber similarly calculated is 3200. The discrepancy between the two results is not entirely unexpected, since deviations from the ideal solution law in other systems are more common than strict adherence. An explanation can be found in the difference in internal pressures and polarity of the constituents.

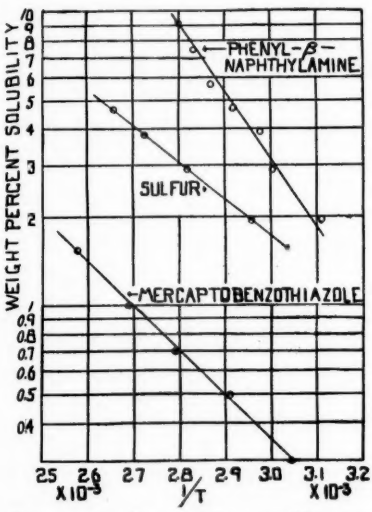

FIGURE 5. PLOT OF LOG OF WEIGHT PER CENT SOLUBILITY *vs.* RECIPROCAL OF ABSOLUTE TEMPERATURE

SUMMARY AND CONCLUSIONS

While a few methods for solubility determination in rubber have been available, they are somewhat difficult and susceptible to large errors. A new method has been developed which has the advantage of being simple, rapid, and accurate, and applicable to all solids soluble in rubber. The apparatus developed can be used for any problem where microscopic observation at elevated temperature will yield information.

The results thus far obtained are of use in explaining the peculiarities of certain organic compounds when used with rubber. It is hoped that sufficient data may be obtained to establish accurately the solubility properties of entire classes of compounds as well as mixtures of several components. In addition to molecular weight determination, the method may yield further results of theoretical interest.

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Experiences with a Direct Accelerator-Adsorption Test

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A method for determining the accelerator adsorption properties of carbon blacks is described. This method is novel in that an extremely dilute solution of diphenylguanidine in benzene is employed. Application of the test to a large number of carbon blacks has revealed its practical value as a measure of those variations in adsorption properties which are of real significance to the rubber manufacturer.

The method has been employed in several separate control laboratories and it has been found to be of distinct value in indicating quality of production. Since the results can be interpreted without knowledge of source or history of the particular carbon black being tested, the test can be employed for control purposes by the rubber manufacturer as well as by the carbon black manufacturer.

THAT the retardation in the rate of cure of a rubber stock resulting from the incorporation of a large percentage of carbon black is due to the adsorptive properties of this extremely fine pigment is a view universally held by rubber technologists. There is a considerable difference of opinion as to what materials are adsorbed.

Historical Data

In 1926 Twiss and Murphy (*10*) expressed a very definite belief that the retardation is due to adsorption of organic

accelerator on the carbon black. In 1928 Dinsmore and Vogt (*2*) stated, "although carbon black and zinc oxide exert the same effect on cure in the sulfur stocks, in accelerated stocks it was necessary to increase greatly the accelerator in the presence of black to approximate the time of cure of the zinc stocks. This shows that the carbon black exerts its greatest effect on the accelerator." In the same article these investigators stated that "carbon black absorbs certain accelerators directly, e. g., heptene, vulcanol... In at least one case—namely, mercaptobenzothiazole—the carbon black affects the cure, apparently due to absorption of the resin acids."

In the same year Goodwin and Park (*5*) write that "adsorption is the one property of carbon blacks that exerts a profound influence upon the character of a rubber mix. It is probably most strikingly shown by a tendency to retard the rate of cure of the mix." They state more specifically that "a highly adsorptive carbon removes the curing agents from the rubber to the extent that it is, for practical purposes, impossible to get a satisfactory gel upon vulcanization," and further that "in the presence of carbon black of the channel type, a larger amount of acid must be present to produce a satisfactory vulcanizate. It behaves as if the stearic acid were removed from the field of action, although the effect is probably more complex."

In 1929 Carson and Sebrell (*1*) mentioned that "it has been noticed for several years, in compounding carbon blacks, that different rates of cure of the rubber stock are obtained with different blacks. The general opinion is that these differences are caused by adsorption of sulfur and accelerator by the blacks..." They compare actual rates of cure with direct adsorption of mercaptobenzothiazole and of diphenylguanidine from one-hundredth normal solutions, and reach the conclusion that "these figures (for direct adsorption) indicate that differences in rate of cure are at least partly due to adsorption of accelerator." Channel blacks and furnace blacks of widely different properties were being compared.

In 1928 Johnson (*6*) made the following statement: "Evidently in the case of high volatile blacks some side reaction with the accelerator occurs which so diminishes its concentration that there is no longer enough to accelerate the vulcanization reaction properly." In the following year (*7*) he studied the accelerator adsorption of Captax and of diphenylguanidine, as well as the volatile content and rubber characteristics of several standard and special channel blacks, and reached the very definite conclusion that the slow cure of blacks with high volatile content was due to physical adsorption of the organic accelerator on the black.

In 1930 Ditmar and Preuss (*3*) noted that highly adsorptive carbon blacks retarded the cure of rubber stocks accelerated

with tetramethylthiouram monosulfide. Since increased sulfur produced overcured stocks, they concluded that the retardation was due to sulfur adsorption and not to accelerator adsorption.

More recently (1931) Drogin (*4*) has described a diphenylguanidine adsorption method for evaluating carbon blacks, and gives results for four selected carbon blacks which indicate that a low adsorption is shown by a faster curing gas black and by a gas black which will give a higher modulus and a higher tensile.

Wiegand (*11*) employed the adsorption of diphenylguanidine from alcohol solution to illustrate the enhanced curing characteristics of some new blacks having low adsorption properties. Wiegand and Snyder (*12*) have applied this adsorption test to a large number of special blacks, as well as to rubber-grade channel blacks. For broad classes of blacks, including some not used in rubber, the correlation between adsorption and rate of cure was very definite for large differences. However, application of the adsorption test to one hundred samples of carbon black of the type normally used in rubber failed to reveal a satisfactory correlation between direct adsorption and modulus. From a study of carbon blacks in litharge stocks, these investigators reach the conclusion that blacks remove, in varying degrees, fatty acids.

Influenced by the work of Stamberger (*9*), which revealed that rubber in solution is adsorbed by carbon black in such a manner as to produce an effect similar to that produced by a slight vulcanization, Lindmeyer (*8*) recently has reached the following novel conclusion: "The early explanation of the fact that gas carbon black, lampblack, colloidal china clay, etc., retard vulcanization because they partly adsorb the accelerator, should be modified; adsorption is chiefly effected through the terminal values of the rubber molecules by the so-called pseudo-vulcanization, and the sulfur atoms have to conquer these valencies."

Discussion

Differences of opinion as to the nature of the adsorption occurring when carbon black is added to a rubber mix may be attributed to the widely varying character of the blacks studied, to the various methods employed for direct measurement of accelerator adsorption, and to the interpretation of the rubber test data. A more extensive application of a given adsorption test to a large number of carbon blacks of standard rubber quality would seem to be quite as desirable as a comparison of different methods of determining adsorption.

About two years ago the writers adopted an empirically developed diphenylguanidine adsorption test as a laboratory control test. The ratio of diphenylguanidine to carbon black in the direct adsorption test was the same as in the case of

the standard diphenylguanidine test formula employed for testing carbon black:

Smoked sheets	93	Zinc oxide	3
Carbon black	35	Sulfur	5
Diphenylguanidine 0.75			

Benzene was originally chosen as the adsorption medium because of its greater similarity to rubber as compared with such solvents as alcohol and water. Because carbon black settles out of suspension in benzene very rapidly, there is a distinct manipulative advantage in using this medium.

In this paper, results typical of those secured in thousands of tests are presented. It is hoped that interpretation of these data in light of the above mentioned studies will lead to a better understanding of the complete action of carbon black in rubber.

Test Procedure

Standard Solutions. (1) 0.001 *M* diphenylguanidine in commercial benzene. Diphenylguanidine (0.211 gram) is dissolved in 1 liter of benzene.

(2) 0.002 *N* alcoholic hydrochloric acid. The hydrochloric acid solution may be standardized against 0.01 *N* sodium hydroxide (water), using phenolphthalein as an indicator.

(3) Bromophenol blue solution. This solution is made by dissolving 0.10 gram bromophenol blue (Tetra Brom Phenol Sulfon Phthalein) in 100 cc. alcohol. Since the bromophenol blue solution is slightly acid, it is neutralized with a few drops of sodium hydroxide solution (about 0.1 *N*). Neutrality is indicated by the appearance of a bluish tone at the surface of the solution when it is agitated, although the main body of it is still red.

Sample. One hundred grams of the black to be tested are thoroughly blended and passed through a 60-mesh screen. From this material a 1-gram sample is taken for the adsorption test.

Procedure. Exactly 1 gram of carbon black is weighed out and transferred to an 8-ounce oil-sample bottle. One hundred cubic centimeters of 0.001 *M* diphenylguanidine solution is then run into the bottle from a buret. The bottle is fitted with a cork stopper, and the contents are shaken for 30 minutes. Thereafter the black is allowed to settle to the bottom of the bottle, which takes from 15 minutes to 1 hour. The clear solution is then poured off into another buret so that 50 cc. will be available. Exactly 50 cc. of the above decanted liquid are run into a suitable size Erlenmeyer flask, and titrated with the 0.002 *N* alcoholic hydrochloric acid using 6 to 8 drops of bromophenol solution as an indicator. The end point of the titration is reached when all traces of blue color have disappeared, and a bright green color obtained. The end point appears to be sharper here than at

the point where a yellow color is reached by a slight further addition of acid.

When compressed carbon black is tested, the black does not settle satisfactorily in the diphenylguanidine solution. In such cases it is necessary to filter or centrifuge.

CALCULATIONS. For all practical purposes, it is considered sufficient to express the result as the percentage of diphenylguanidine adsorbed. When this method of calculating is used, it is not really necessary to know the exact normality of the solutions, although it is essential to make them up carefully to the desired strength so as to eliminate error due to concentration effects.

The percentage adsorption is calculated from the decrease in strength of the diphenylguanidine solution as indicated by the equivalent amounts of standard acid solution used in blank and test runs:

A = percentage adsorption
B = acid used in blank titration, cc.
C = acid used in test run, cc.

where

$$A = \frac{B - C}{B} \times 100$$

APPLICATION OF TEST TO RUBBER BLACKS

The adsorption test was applied to a large number of channel-process carbon blacks whose behavior in rubber were known. The results given in Table I are typical for rubber blacks having widely varying curing characteristics. It may be observed that the ultra rapid curing characteristic of the devolatilized special carbon black, Carbaccel, is indi-

TABLE I. STANDARD DIPHENYLGUANIDINE TEST FORMULA

PERIOD OF CURE[a]	CARBACCEL BLACK	PLANT A BLACK	PLANT D BLACK	POOR BLACK	NO. 11 BLACK	VERY POOR BLACK
Minutes	TENSILE AT BREAK (kg./sq. cm.)					
20	333	271	262	202	174	98
30	336	294	300	238	199	127
40	324	319	303	265	226	134
60	304	314	317	285	279	148
80	286	296	304	285	290	163
	LOAD AT 400% (kg./sq. cm.)					
20	184	100	83	69	56	29
30	197	132	118	90	74	44
40	228	160	138	111	84	66
60	250	186	162	130	117	75
80	247	193	181	148	116	86
	HARDNESS (SHORE)					
20	65	57	55	52	53	40
30	68	62	60	55	56	45
40	70	65	63	58	58	50
60	72	68	67	60	62	53
80	73	70	68	62	65	55
	VOLATILE CONTENT (%)					
..	2.32	4.55	4.26	6.35	6.19	10.74
	IODINE ADSORPTION (%)					
..	15.6	12.0	12.6	14.3	14.9	17.1
	DIPHENYLGUANIDINE (%) ADSORPTION					
..	16.9	24.8	33.7	58.3	52.8	100

[a] At 141.5° C.

cated by the very low accelerator adsorption. Likewise the abnormally slow-curing blacks are indicated by high accelerator adsorption. The relatively slight difference in rate of cure between samples from Plant A and Plant D, which is shown by the modulus and hardness figures, is reflected in the direct adsorption percentages.

That the adsorption of diphenylguanidine is specific is proved by the corresponding percentages for iodine adsorbed from 0.1 *N* iodine in potassium iodide solution. In the case of abnormally fast and slow blacks the volatile content seems to be a measure of the rate of cure characteristics of carbon blacks. Experience with thousands of volatile matter tests has revealed the fact that volatile matter can be interpreted in terms of rubber characteristics only when the individual plant conditions are definitely known.

TABLE II. PHYSICAL DATA, LITHARGE STOCKS

Period of Cure[a]	Carbaccel Black	Plant A Black	Plant D Black	Poor Black	No. 11 Black	Very Poor Black
Minutes						
	TENSILE AT BREAK (kg./sq. cm.)					
10	231	187	186	229	...	191
20	289	251	255	267	257	267
30	314	277	288	318	312	324
40	339	307	306	343	318	325
50	344	333	327	352	323	330
	LOAD AT 400% (kg./sq. cm.)					
10	73	46	46	62	...	71
20	110	63	73	92	98	110
30	134	100	93	120	131	141
40	170	113	123	158	159	176
50	174	146	149	160	166	178
	HARDNESS (SHORE)					
10	51	45	48	48	..	50
20	55	50	53	53	55	55
30	58	55	57	57	58	58
40	62	57	59	60	61	62
50	64	59	61	60	63	63

[a] At 134.5° C.

In Table II are the results of rubber tests on these same carbon blacks in litharge stocks. This inorganic accelerator is used so that adsorption of dissolved accelerator by the carbon black will be minimized. The formula used was:

Smoked sheets	100	Sulfur	4
Carbon black	38	Pine tar	2
	Sublimed litharge	10	

It is apparent that all of these carbon blacks possess inherently good reënforcing properties. The great similarity between Carbaccel and very poor black is particularly striking in view of the extreme differences shown when diphenylguanidine formula was used. The results form additional evidence that rate of cure of rubber blacks is dependent mainly on the adsorption of accelerator.

USE AS PLANT CONTROL TEST

To gain some knowledge of the value of the diphenylguanidine adsorption test as a control in the manufacture of carbon black, this test was applied to samples received

from several manufacturing plants in March, 1930. The adsorption percentages may be compared with the modulus figures of the standard rubber test (diphenylguanidine formula) in Table III. Both the direct adsorption test and the standard rubber test indicated a faster rate of cure for the carbon black being made at Plant E at that time. The moduli for the two cures do not always serve as accurate measure of the rate of cure, but space does not permit a tabulation of the complete rubber test results. The experimental error in the modulus figures is high, because the stocks were not remilled, and no master batch was used.

TABLE III. USE OF ACCELERATOR ADSORPTION TEST FOR CONTROL PURPOSES

SAMPLE	DIPHENYL-GUANIDINE ADSORBED	LOAD AT 400% 20-min. cure	LOAD AT 400% 40-min. cure
	%	*Kg./sq. cm.*	*Kg./sq. cm.*
	PLANT E		
2641	21.7	...	178
2674	22.6	...	179
2736	24.3	113	160
2745	23.1	120	162
2750	24.3	122	169
2769	24.9	123	160
2770	19.3	123	162
2777	26.4	112	157
2778	27.5	120	152
2781	24.2	117	149
2790	22.5	121	164
2797	23.5	130	170
	PLANT D		
2737	29.6	101	151
2738	29.7	104	150
2779	30.6	108	145
2780	30.6	112	148
	PLANT F		
2742	31.3	104	150
2782	32.5	111	146
	PLANT C		
2746	34.2	97	147
2747	29.4	111	152
2748	30.7	102	147
2749	30.1	106	152
2793	33.9	113	156
2794	32.0	110	155
2795	29.2	106	151
	PLANT B		
2751	42.2	95	142
2752	30.5	104	152
2753	31.2	98	141
2757	25.3	99	139
	PLANT A		
2775	30.7	104	150
2776	25.5	104	157

Although average results appeared to be truly indicative of quality, individual adsorption percentages varied considerably without corresponding change in rate of cure. In the light of later tests a considerable part of this variation may be attributed to failure to obtain truly representative samples. So thorough appeared the stirring of the carbon black in the numerous screw conveyors, the air separators, and the agitating tank, that at first no effort was made to blend the sample taken at the packer. Later investigations revealed that, in a gallon-can sample of carbon black taken at the packer,

TABLE IV. SUMMARY OF DIPHENYLGUANIDINE ADSORPTION TESTS ON PLANT B

Samples received November, 1930

SAMPLE	DIPHENYLGUANIDINE ADSORBED			LOAD AT 400%[a]
	Plant B lab.	Boston lab.	Difference	
	%	%	%	*Kg./sq. cm.*
3237	36.0	34.7	1.3	82
3238	31.2	33.5	2.3	77
3239	31.6	34.1	2.5	77
3247	32.5	35.0	2.5	90
3248	37.8	39.4	1.6	82
3249	35.4	36.1	0.7	84
3250	37.7	35.0	2.7	87
3252	33.0	33.5	0.5	90
3253	35.0	35.2	0.2	90
3254	34.2	35.5	1.3	82
3259	35.1	35.0	0.1	87
3260	37.0	34.4	2.6	78
3261	34.1	32.2	1.9	82
3262	33.0	32.7	0.3	87
3269	35.2	34.3	0.9	92
3270	33.3	32.7	0.6	88
3272	33.6	32.7	0.9	77
3275	35.4	31.8	3.6	78
3276	34.0	34.6	0.6	84
3277	34.8	33.9	0.9	84
3280	36.2	35.4	0.8	80
3281	34.8	32.9	1.9	81
3282	38.2	36.2	2.0	82
3284	33.0	36.7	3.7	87
3285	31.9	34.8	2.9	84

[a] 20-minute cure.

TABLE V. COMPARISON OF SEVERAL CONTROL TESTS

SAMPLE	VOLATILE CONTENT	DIPHENYLGUANIDINE ADSORBED		LOAD AT 400%	
		Plant lab.	Boston lab.	20-min. cure	40-min. cure
	%	%	%	*Kg./sq. cm.*	
		PLANT D			
3739	4.18	32.1	31.9	94	129
3743	4.19	32.3	31.6	91	143
3754	4.51	30.8	30.9	80	126
3770	..	30.2	32.4	99	136
3740	4.08	32.0	34.1	87	128
3755	4.35	33.7	34.7	87	133
3771	..	32.4	34.9	90	134
		PLANT B			
3751	4.83	28.0	31.2	89	119
3765	5.09	29.4	27.1	98	144
3766	5.13	29.8	26.5	95	129
3767	5.08	29.6	27.4	89	129
		PLANT C			
3734	4.62	24.0	25.0	102	150
3747	4.68	28.8	31.5	98	138
3761	4.13	30.0	34.3	101	148
3735	4.98	28.4	29.5	92	142
3748	4.85	27.7	30.3	92	128
3762	4.84	26.4	29.8	90	134
3736	4.91	28.4	28.4	95	134
3749	5.17	26.5	30.8	96	129
3763	5.09	27.7	30.8	99	136
		PLANT F			
3738	4.45	..	34.8	86	125
3750	4.50	..	36.9	99	122
3760	4.14	..	36.3	84	120
3756	4.26	..	34.2	78	111
3773	3.78	..	33.5	87	127
		PLANT A			
3741	4.54	..	26.5	92	135
3745	4.49	..	27.9	95	141
3757	4.28	..	25.8	87	126
3768	..	..	27.1	87	130
3742	4.68	..	25.4	100	143
3746	4.67	..	28.5	91	130
3758	..	..	29.6	91	139
3769	4.54	..	27.1	94	139

the accelerator adsorption would vary from top to bottom by several per cent. In case of all adsorption tests reported below, special precautions were taken to secure a thorough blend of sample.

Since tests made over a period of months in the laboratories in Boston indicated a close correlation between diphenylguanidine adsorption and actual rate of cure, this adsorption test was adopted as a control test by the plant control laboratory at Plant B. In Table IV appear the adsorption results obtained by both laboratories and the modulus figures from

TABLE VI. CORRELATION OF AVERAGE PLANT ADSORPTION PERCENTAGES WITH MODULUS VALUES

PLANT	LOAD AT 400%[a]	ADSORPTION[b]
	Kg./sq. cm.	%
A	113	27.2
B	111	28.1
C	113	30.0
D	111	32.9
F	104	35.1

[a] 20- and 40-minute cures.
[b] Boston laboratory.

TABLE VII. EFFECT OF HIGH ACCELERATOR ADSORPTION ON RATE OF CURE

(Standard diphenylguanidine test formula)

PERIOD OF CURE[a]	SAMPLE						
Minutes	3235	3333	3775	3047	3048	3120	3131
	TENSILE AT BREAK (kg./sq. cm.)						
20	270	225	203	176	178	156	168
40	327	307	336	273	254	233	192
60	335	314	311	292	277	259	229
	ELONGATION AT BREAK (%)						
20	690	657	663	660	690	680	700
40	655	650	640	640	660	630	600
60	620	615	635	630	600	630	590
	LOAD AT 400% (kg./sq. cm.)						
20	83	71	66	57	60	43	47
40	132	121	107	110	99	93	84
60	157	151	113	135	126	102	108
	HARDNESS (SHORE)						
20	58	56	54	53	53	50	51
40	65	61	58	60	58	58	58
60	69	66	62	65	63	61	61
	DIPHENYLGUANIDINE ADSORPTION (%)						
..	40.9	39.4	39.1	39.6	53.3	57.8	60.8
	VOLATILE CONTENT (%)						
..	3.46	5.08	5.80	5.94	6.37	6.38	6.76

[a] At 141.5° C.

the standard rubber tests for twenty-five samples tested in November, 1930. The maximum difference in adsorption percentages between the two laboratories seems to be about one-half the maximum difference in adsorption which occurs when carbon black of uniform rubber characteristics is being produced.

Later the diphenylguanidine adsorption test was adopted at other plants. Tests were made several times each day, and selected samples submitted to the Boston laboratory of Godfrey L. Cabot, Inc., for rubber tests and checks on the

plant adsorption test. Table V contains a tabulation of data secured during the period between June 18 and July 18, 1931.

The variations in quality must be admitted to be very small when the extreme sensitiveness of the rubber test and of the adsorption test is taken into consideration. There

TABLE VIII. FAST- AND SLOW-CURING BLACKS, STANDARD DIPHENYLGUANIDINE TEST FORMULA

Physical data

Period of Cure[a] Minutes	Tensile Kg./sq. cm.	Elongation %	Load at 400% Kg./sq. cm.	Hardness (Shore)
		Bag 6		
30	306	640	134	62
40	319	620	161	66
60	294	553	183	69
80	293	523	199	71
		Bag 4		
30	202	607	90	56
40	258	645	106	59
60	279	625	130	62
80	279	590	142	64

Chemical data

	Diphenylguanidine Adsorbed %	Volatile Content %
Bag 6	39.4	3.98
Bag 4	46.9	7.50

[a] At 141.5° C.

TABLE IX. FAST- AND SLOW-CURING BLACKS, CAPTAX TREAD STOCKS

Black Master		Final Mix	
Smoked sheets	51.0	Black master	86.0
Whole-tire reclaim	12.0	Smoked sheets	10.0
Carbon black	30.5	Captax	0.25
Zinc oxide	3.5	Sulfur	1.75
Agerite resin	0.5	Stearic acid	2.0
Pine tar	2.5		
	100.0		100.0

Period of Cure[a] Minutes	Tensile Kg./sq. cm.	Elongation %	Load at 400% Kg./sq. cm.	Hardness (Shore)
		Bag 6		
20	213	703	77	67
30	263	710	103	72
45	258	655	118	75
60	268	625	134	76
90	257	600	145	78
		Bag 4		
20	172	670	65	61
30	230	710	80	66
45	260	680	109	69
60	268	670	122	71
90	253	610	134	73

[a] At 134.5° C.

is an indication that the carbon black produced at Plant F was somewhat slower curing. This is better shown by the average figures in Table VI, which are obtained from the data in Table V. The data for volatile content are included to show that there were no marked variations in this value.

Significance of Variations in Adsorption

Since in the case of individual blacks the diphenylguanidine adsorption may vary from about 27 to 37 per cent with no change in rubber quality, the question arises: At what adsorption percentage do all carbon blacks appear definitely inferior in quality? The data in Table VII indicate that carbon black with an adsorption of more than 50 per cent is definitely slow in rate of cure, and that carbon black with an adsorption of 40 per cent may be slow, particularly if the volatile content is high. In no case has a carbon black with an adsorption of less than 40 per cent been found which has had a definitely slow rate of cure.

Tests made two years ago on two samples of carbon black received from a rubber company are of interest as exhibiting the relationships existing in direct adsorption test, volatile content, laboratory-control rubber test, and tire-tread compound test. The results are assembled in Tables VIII and IX.

Table X. Data on Standard Diphenylguanidine Test Formula

Physical data

Period of Cure[a] *Minutes*	Tensile *Kg./sq. cm.*	Elongation %	Load at 400 % *Kg./sq. cm.*	Hardness (Shore)
		Black 3774		
20	250	655	92	57
40	298	637	134	62
60	304	593	162	66
		Black 3775		
20	203	663	66	54
40	336	640	106	58
60	310	635	131	62

Chemical data

Black	Diphenylguanidine Adsorbed %	Volatile Content %
3774	24.7	5.40
3775	39.1	5.80

[a] At 141.5° C.

The more highly adsorptive carbon black produces a softer stock with lower modulus. The effect is probably somewhat unusual in case of the tread stock, since use of alkali reclaim and Agerite resin permits use of a very low percentage of Captax. Use of a higher percentage of Captax (or of any other accelerator) should lessen the effect of the carbon black. The data in Tables X and XI furnish proof of this point.

Application of Test to Special Carbons

During the course of this work on accelerator adsorption, a large number of pigment carbons have been studied. Typical results are given in Table XII, and these furnish evidence that this new direct adsorption test can be employed with all those pigments which are essentially different forms of carbon. The rates of cure indicated by tensiles are in harmony with the rates of cure indicated by the adsorption

test. Owing to the great differences in particle size of these pigments, the rates of cure are not indicated by the modulus or hardness data. In fact, these results furnish very convincing evidence that the accelerator adsorption test indicates rate of cure only, and not inherent tensile or modulus characteristics.

TABLE XI. PHYSICAL DATA, CAPTAX FORMULA

Smoked sheets	60.6
Carbon black	30.5
Zinc oxide	4.75
Sulfur	1.7
Stearic acid	2.0
Captax	0.45
	100.00

PERIOD OF CURE[a] *Minutes*	TENSILE *Kg./sq. cm.*	ELONGATION %	LOAD AT 400% *Kg./sq. cm.*	HARDNESS (SHORE)
		BLACK 3774		
20	232	580	127	62
40	285	580	169	68
60	300	550	191	70
		BLACK 3775		
20	228	613	108	62
40	286	587	166	68
60	288	560	187	70

[a] At 138° C.

TABLE XII. ACCELERATOR ADSORPTION PROPERTIES OF VARIOUS CARBONS

(Standard diphenylguanidine test formula)

PERIOD OF CURE[a] *Minutes*	P-33 CARBON	GASTEX BLACK	ACETYLENE BLACK	LAMP BLACK	PAINT BLACK	PAINT BLACK DEVOLATILIZED
	TENSILE AT BREAK (kg./sq. cm.)					
20	302	268	263	195	153	298
40	283	252	254	212	236	312
60	254	248	270	228	250	296
	ELONGATION (%)					
20	707	560	660	567	630	640
40	623	477	580	520	680	603
60	580	440	580	530	615	563
	LOAD AT 400% (kg./sq. cm.)					
20	79	148	103	108	47	114
40	121	191	123	145	72	149
60	130	216	144	155	96	163
	HARDNESS (SHORE)					
20	53	55	58	55	55	62
40	58	62	63	58	61	68
60	60	65	67	62	65	70
	DIPHENYLGUANIDINE ADSORPTION (%)					
..	0.0	6.1	7.30	17.5	82.6	23.3
	VOLATILE CONTENT (%)					
..	0.50	0.53	1.15	4.52	4.77	1.93

[a] At 141.5° C.

The volatile contents of these carbons are typical. Reduction in the volatile content of a given carbon has always resulted in an increase in rate of cure. Carbons with extremely low volatile content are fast-curing. In the case of carbon pigments which are essentially different in properties and characteristics, the volatile content is not even an approximate measure of the accelerator adsorption properties.

Literature Cited

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Effect of Curing Temperature on Quality of Vulcanized Rubber

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A review of the literature permits no definite conclusion concerning the influence of temperature of vulcanization on the ultimate quality of a rubber product. Some investigators claim equal properties at different curing temperatures, others superior properties at low temperatures, while still others believe superior qualities are obtainable at higher temperatures. Concerning the influence of temperature on aging, no conclusive data are available.

The temperature of cure has no influence on the tensile properties at maximum, in the case of the di-o-tolylguanidine stock. In the case of the mercaptobenzothiazole stock, there is a trend toward slightly higher tensile strength as the temperature is decreased.

Natural, as well as artificial, aging of the di-o-tolylguanidine stock shows that the lower the temperature of cure, the better the aging will be. The results are clean-cut, probably owing to the fact that this is a stock which ages rapidly and hence shows differences in comparatively short periods of aging.

The data on the mercaptobenzothiazole stock containing an antioxidant are far from conclusive, though they show a trend toward better aging with lower temperatures of curing.

THE effect of curing temperature on the quality of vulcanized rubber has been a moot question for many years, especially since the advent of organic accelerators, which permit rapid curing at comparatively low temperatures. In the old days, when the rubber technologist had at his disposal only such materials as litharge, lime, or magnesia for the acceleration of his stocks, a curing temperature below that corresponding to 40 pounds steam pressure (287° F. or 141.5° C.) was impractical. It was common practice to use even higher temperatures (50 pounds, corresponding to 298° F. or 148° C., or above) in order to increase the output per curing unit. The organic accelerators available at present permit curing at temperatures as low as 15 pounds steam pressure (250° F. or 121° C.), as, for example, with one of the thiuram mono- or disulfides; or 25 pounds pressure (266.5° F. or 130° C.), as, for example, with mercaptobenzothiazole, in a length of time which is commercially practical. This is true even in the case of such large thick articles as automobile tires. With the former type of organic accelerator, a small tire, such as a 4.75, may be cured in 1 hour; and with the latter material (mercaptobenzothiazole), in almost the same length of time, provided a sufficient concentration of accelerator is supplied. With the larger sizes of tires, of course, the time must be increased to a very considerable extent, in order to obtain the proper cure in the plies and at the base of the tread.

What is gained by using such active accelerators is a question worthy of serious consideration. Their use necessitates very careful processing in the factory to avoid scorching during the milling, tubing, and calendering operations, and requires the installation of expensive equipment for rapid cooling after each operation. Once it has been learned how to incorporate these materials successfully, the question of curing temperature constantly arises, even though the curing time at low temperature is no longer than that of the stock which the new and faster compound may have replaced. A higher temperature will mean shorter cures, and pressure for production is often the deciding factor in raising the temperature. The question thus becomes one of cost *vs.* quality, and that latter point has never been conclusively settled. Technologists have glibly stated as a commonplace that "of course, low-temperature curing means added quality. Heat is detrimental to rubber. There is no room for argument." A search of the literature reveals nothing to substantiate such statements definitely. It is true that certain accelerators have produced remarkable physical properties in stocks cured at low temperatures, as compared with the products obtained with other accelerators at higher temperatures of cure. Here the specific action of the accelerator in improving quality is involved, and it is difficult to differentiate between this effect and that of the curing temperature itself.

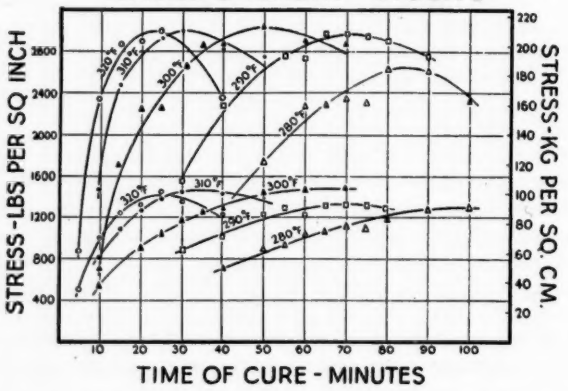
Unfortunately, only a small amount of data has been published in which one and the same rubber mix has been

cured for different intervals of time at different temperatures. This is especially true as regards mixes containing organic accelerators. The literature does afford a considerable number of statements unsupported by experimental evidence, and a few supported by satisfactory data, with reference to rubber-sulfur mixes. This published work deals chiefly with the effect of curing temperature on the initial properties of the vulcanized rubber. In some cases the stability or aging qualities *vs.* temperature of cure have been studied. Both of these aspects of the subject have been covered in the literature search and are discussed chronologically before presenting new data.

Previous Investigations

The elder Weber (*18*) has stated that "the same degree of vulcanization, as expressed in percentage of combined sulfur, may be obtained by (1) short vulcanization at high tempera-

FIG 1-INITIAL MODULUS AND TENSILE STRENGTH - STOCK I



ture with high sulfur; (2) slow vulcanization at lower temperature with small additions of sulfur; or (3) a temperature slowly rising to a maximum; but in every case the properties of the vulcanizates differ more or less considerably." He does not state whether or not the lower temperatures gave superior physical properties.

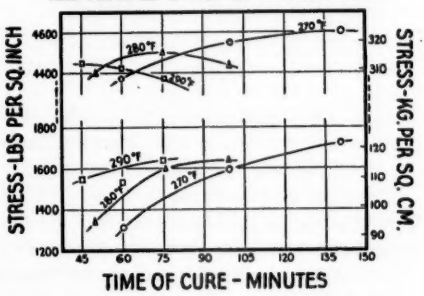
Bobet (*2*) was of the opinion that lower temperatures of vulcanizing were favorable to a higher quality. He specified 128–130° C. (262–266° F.) as a desirable curing range, with 135–140° C. (275–284° F.) as less satisfactory, as it generally resulted "in detriment to the quality of the product." He believed a curing temperature of 150° C. (302° F.) to be detrimental to rubber, especially to certain grades.

Breuil (*3*) concluded from his experiments in 1906 that high temperature diminishes the tensile properties and elongation much more than a somewhat longer time of curing at a lower temperature. It seemed to him, as to Bobet, that there was

an optimum temperature, but he selected a higher temperature (140° C. or 284° F.) for the mixtures which he studied. These contained 2.5, 5.0, 7.5, and 10.0 per cent of sulfur, but the data concerning the properties obtained at the different temperatures (130°, 140°, 145°, and 150° C., or 266°, 284°, 293°, and 302° F.) are inconclusive with reference to quality, as no range of cures at the different temperatures was presented. It is thus not known whether the cures compared were those giving maximum properties. From the curing periods selected for comparison, it is quite certain that they were not in any sense equivalent.

During the following year, Ditmar (*6*) published an extensive series of results obtained on rubber-sulfur mixes containing 4 per cent of sulfur. Fine Para was compared with several other types of rubber, including Upper Congo, Bassam lumps, and guayule, using curing temperatures corresponding to 4 atmospheres (44 pounds steam pressure, or approximately 292° F.), and 15 atmospheres (206 pounds steam pressure or 390° F.), respectively. From a historical standpoint if for no other reason, this work has considerable interest, for, as far as the writers are aware, this latter is by far the highest vulcanizing temperature recorded in the literature. In fact, one would assume that no satisfactory properties could be obtained at any such degree of heat, for rubber decomposes at atmospheric pressure at a temperature only slightly above this.

FIG. 2 - INITIAL MODULUS AND TENSILE STRENGTH - STOCK II A

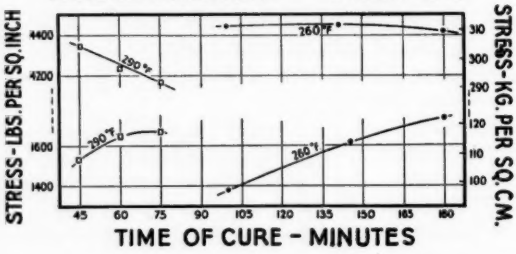


Unfortunately Ditmar chose, for his comparison of the influence of temperature, cures which could not possibly have been equivalent. For example, among the fine Para samples he selected the 30-minute cure at 292° F. or 144.4° C. (combined sulfur 1.1 per cent) for comparison with the 10-minute cure at 390° F. or 198.9° C. (combined sulfur 3.8 per cent). These cures had approximately the same tensile properties, as did also the pairs of cures chosen for comparison of the other rubbers. There was no correlation between the tensile values and the temperature of cure. From this, Ditmar concluded that there was no difference worth mentioning in the initial properties obtainable at the two widely separated temperatures. However, he was led erroneously to conclude, from the increase in weight of the samples when subjected to his oxygen aging test at 100° C., that the lower temperature

produced products of markedly superior aging quality. It is obvious that this result was due to the advanced chemical state of cure, rather than to any specific influence of the temperature.

Axelrod (*1*) has published definite and convincing data confirming Weber's views on the properties obtainable when curing to the same combined sulfur at different temperatures. He writes: "The important conclusion must be drawn that one and the same mixture of rubber and sulfur, vulcanized at different temperatures, must give products of different physical properties, even if the quantity of combined sulfur is the same. This difference manifests itself in higher extensibility at the same load or, conversely, in lower load for the same elongation in cases of vulcanization at higher temperature." Seidl (*14*) commented adversely on Axelrod's conclusions, stating that his results "are not in accord with the results of other investigators and practical experience." Seidl takes exactly the opposite view concerning curing at higher temperatures, claiming that for the same combined

FIG 3 - INITIAL MODULUS AND TENSILE STRENGTH - STOCK II B

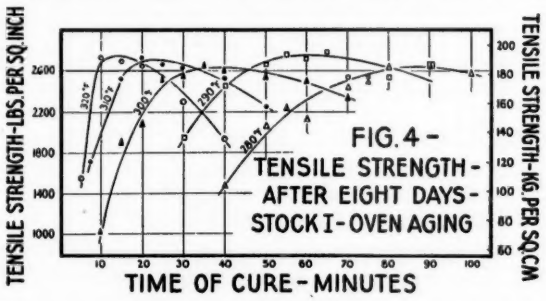


sulfur, higher properties must result, since a lesser depolymerization occurs during the short vulcanization time required when a high temperature is employed. He bases this conclusion on the work of Gottlob (*7*), who used "Vulkacit," presumably aldehyde-ammonia, as his catalyst. No differentiation can be made in this work between the specific effect of the accelerator and that of the temperature.

In 1911 Breuil (*4*) presented further data which have a bearing on this subject. Curing was carried out at 135° C. (275° F.) and 145° C. (293° F.). Unfortunately the curing at 135° C. was in no case continued until a peak or optimum in the tensile strength curve was clearly defined, so that no comparison of the maximum tensile properties at the two temperatures can be made. With our present knowledge of temperature coefficients, it is difficult to accept the cures selected by Breuil as equivalent. How he picked these is not clear.

While not agreeing with Seidl that higher curing temperatures are beneficial to quality, Kratz (*9*) felt that higher temperatures of cure could be used advantageously in shorten-

ing the curing period without detriment to the product. In his work he used 5 parts of sulfur to 100 parts of rubber and 100 parts of zinc oxide. His curing temperatures ranged from 36 pounds steam pressure (282° F. or 139° C.) to 85 pounds (327° F. or 164° C.) at approximately 5-pound intervals. The periods of cure ranged from 120 minutes at 36 pounds to 8 minutes at 85 pounds. The correct cures were picked by the "thumb and tooth test," as he calls it. He concludes that up to 70 pounds steam pressure (316° F. or 158° C.) there is no discrepancy either in tensile strength or elongation, other than that which might be attributed to experimental error. As a matter of fact, the tensile figures for the "correct" cures at the ten different temperatures did vary considerably (from 2545 to 3064 pounds per square inch, with an average figure of 2800) but in no definite direction. That Kratz was quite successful in picking his cures was indicated by the smoothness of the curve obtained by plotting steam pressures against time at which the "correct" cures were obtained. While Kratz does not present his aging figures, he states that "the various samples showed equal



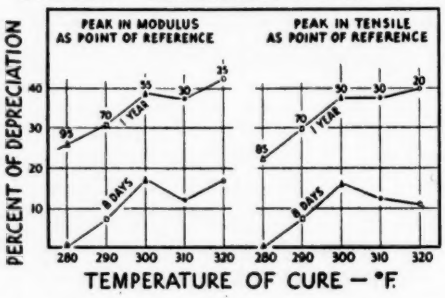
abilities to withstand the effects of air, sunlight, and time." However, the aging period was only 4 months, in which period there was "no appreciable deterioration in any of them." In the writers' opinion this was far too short a period of aging upon which to conclude that "if a compound is correctly vulcanized, the temperature at which it is vulcanized in no way affects its aging properties."

King (*8*) has accepted Seidl's view that higher temperature of cure gives superior properties. He states: "It was formerly held that high temperatures were harmful, and so they are when the nature of the article is such that heat flow is very slow, but whenever the piece can be brought to press temperature, through and through, in a very short time, a higher temperature for a shorter time produces a better article than a lower one for a longer time."

Kratz (*10*) also studied the effect of vulcanizing at a constant temperature *vs.* vulcanizing at a series of increasing temperatures (a "raised" cure). He reached the conclusion that, for the particular mixing studied (rubber 100, zinc oxide 100, sulfur 5, and an undivulged organic accelerator 0.33), the

physical properties were superior when it was vulcanized at a series of increasing temperatures. If this were true, it would indicate superiority of low over high temperature of cure, but Kratz's figures are not convincing to the writers. In one case, curing to a sulfur coefficient of 2.9, a tensile strength of 2160 pounds per square inch was obtained at a constant temperature (120 minutes at 298° F. or 148° C.), as against 2230 pounds per square inch with a rising temperature (107 minutes at 285.5° F. or 141° C., 60 minutes at 298° F. or 148° C., and 13 minutes at 302.5° F. or 150° C.). These figures are certainly well within experimental error. Another example was given (curing to the high coefficient of 3.9) which gave contrary results in that it showed a definite superiority (500 pounds per square inch) for the "raised cure." From the writers' study of this paper, it is their opinion that the data do not warrant the conclusion that a rising temperature is advantageous from a quality standpoint, especially as the difference was only shown on a serious over-

FIG. 5 - PERCENTAGE CHANGE IN TENSILE STRENGTH vs. TEMPERATURE OF CURE - STOCK I



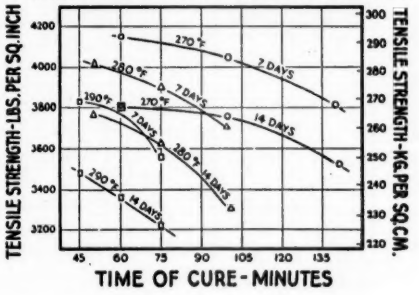
cure, which was at least 1 hour and 30 minutes beyond the cure of maximum tensile strength, and 3 hours beyond Kratz's selected "best technical cure." However, Kratz did present figures for this mix cured to "correct technical cure" at both 298° F. (148° C.) and 285.5° F. (141° C.). These were equal within probable experimental error. The two values were 2280 and 2170 pounds per square inch, respectively; the sulfur coefficients were 1.69 and 1.57. The aging of these samples was not discussed.

Apparently de Vries (*17*) was as little convinced by the conflicting conclusions of the above investigators as are the writers, for he concluded in writing on this subject in 1920: "In how far the temperature of vulcanization has an influence on the mechanical properties of rubber is not yet settled."

Since that time there have been additional data and opinions published on this subject. Twiss and Brazier (*16*) cured a rubber-sulfur mix (rubber 100. sulfur 10) at 138°, 148°, 158°, and 168° C., respectively. The maximum tensile-strength figures were not increased by reducing the curing temperature.

Perks (*13*), in England, is apparently convinced that curing temperature in itself is of little importance as regards the quality of a rubber product, for he goes so far as to state that "it is possible to secure practically equal service from tires cured at either 149° C. (300° F.), 154° C. (309° F.), or 160° C. (320° F.) by the proper choice of the compounds involved." No data were presented. This opinion is not generally held in this country, where temperatures above Perks' lowest specified temperature are seldom used in curing tires. Dinsmore (*5*) expressed the opinion, during the discussion of his paper on "A Scheme of Accelerator Classification," that the lower the temperature of vulcanization, the less was the likelihood of a stock suffering a reduction in tear resistance after aging.

FIG 6.-TENSILE STRENGTH AFTER ACCELERATED AGING (GEER OVEN)-STOCK II A

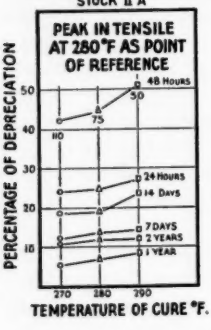


The work of Stoll (*15*) leads to the conclusion that moderate temperatures are desirable in curing tires, on the basis of fabric depreciation if for no other reason. Up to a temperature of 110° C. (230° F.), his experiments with cords of 12/3/3 construction showed that the loss in strength and elongation was small, while at 140–150° C. (284–302° F.) for 2 hours, the loss in strength was approximately 15 per cent. Even heating for 15 minutes at 150° C. (302° F.) resulted in a loss of 13 per cent in strength. Unfortunately, the author does not state how he conditioned the cords after heating and before testing.

In this field the latest contribution with which the writers are familiar is that of Park (*11*). His work dealt with the behavior of a rubber-sulfur mix (unaccelerated), containing 100 parts of rubber and 6.25 parts of sulfur. The vulcanizing temperatures ranged from 135.5° C. (276° F.) to 162° C. (324° F.), with a curing time of 360 minutes at the former temperature and 27 minutes at the latter, for the "optimum equivalent" cures, as judged by stress-strain data and hand examination. Comparison of these cures and the corresponding ones at the intermediate curing temperatures, leads to the conclusion that the initial physical properties of the optima were approximately equal. As the author points out, there was a slight downward trend with increasing temperature of cure, but he concluded that this was caused entirely by random variation. Natural aging of these samples, so

nearly equal in initial tensile properties, resulted in no greater depreciation, after 3 years, in the samples cured at the higher temperatures than in those cured at lower temperatures. However, it should be noted that all the cures selected aged remarkably well, appreciation in tensile properties having occurred in every case up to 2 years, with only slight depreciation from the high 2-year value at the end of 3 years. In every case the 3-year tensile figures were at least 40 per cent higher than the initial values. However, artificial aging both in air at 70° C. (Geer) and in oxygen at 60° C. (Bierer-Davis) showed no great differences, or correlation with the temperature used in curing. Park's conclusion was that no broad generalization as to the effect of curing temperature on properties could be drawn, but that for the specific rubber-sulfur mix, within the temperature range investigated, the temperature of cure had no effect on the quality of the vulcanized stock. He concluded that improved physical properties encountered in low-temperature curing, if there are any, must be caused by other compounding ingredients, "accelerators probably playing the most important part."

FIG 7–
PERCENTAGE CHANGE IN TENSILE STRENGTH ON AGING VS. TEMPERATURE OF CURE
STOCK II A



From this summary of the literature, the writers conclude that it has been established quite definitely that the temperature of cure, in the case of a rubber-sulfur mix, has little influence on the initial properties, provided really equivalent cures are compared. There certainly is no justification for the unsupported statements that higher curing temperatures are superior to lower temperatures from the standpoint of rubber quality. The data supporting the claim of superiority for low-temperature cures are weak, and cannot be given much credence.

As regards accelerated mixes, there are no available data of importance on the effect of different temperatures of cure. Kratz gave figures which indicated equivalent initial properties at two different curing temperatures, but his work lacks significance because the nature of the accelerator was not divulged.

The evidence that the aging qualities are independent of the curing temperature is not considered conclusive, as no natural aging data have been presented which cover the history of the samples over a period sufficiently long to show marked depreciation from the initial properties.

The contribution of the writers to this subject consists in a study of rubber stocks which were cured in the presence of organic accelerators. As Park has intimated, such stocks should be of greater interest than simple rubber-sulfur mixes.

One of these stocks contained di-*o*-tolylguanidine, and the other mercaptobenzothiazole. The former contained reclaim and no antioxidant, and may be classed as a stock of only moderately good aging qualities. The latter contained an antioxidant (aldol-α-naphthylamine) and is classed as a stock of superior aging resistance. While the results of the tests recorded and discussed in the experimental part of this paper are not as extensive as might be desired, they show, in the writers' opinion, a definite tendency toward better aging when lower temperatures are used in curing, though no marked difference in the initial properties was found. These data are presented with the hope that they will lead to the publication of similar and more comprehensive data by others.

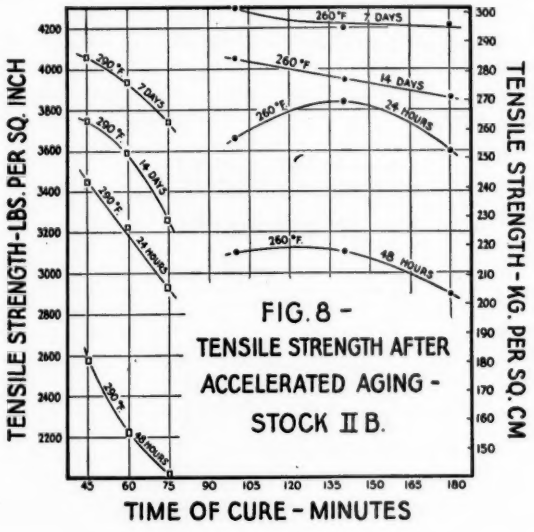


FIG. 8 - TENSILE STRENGTH AFTER ACCELERATED AGING - STOCK II B.

Experimental Procedure

The formulas used in these tests were those of the typical tread stocks, I and II.

Stock I[a]	*Parts*	Stock II	*Parts*
Smoked sheets	28.3	Smoked sheets	100
Amber blankets	44.8	Carbon black	42
Whole tire reclaim	44.8	Zinc oxide	6
Carbon black	33.3	Stearic acid	3.5
Zinc oxide	14.0	Pine tar	4
Pine tar	5.3	Aldol-α-naphthylamine	1
Sulfur	2.9	Sulfur	2.75
Di-*o*-tolylguanidine	0.6	Mercaptobenzothiazole	0.75
	174.0		160.00

[a] The rubber content, including the hydrocarbon of the reclaim, totals 100 parts.

The methods of mixing, curing, and testing were those regularly employed by rubber technologists.

Standard methods of artificial aging were used, including the Geer heat test at 70° C. (158° F.), and the Bierer-Davis

bomb test, using a temperature of 70° C. with oxygen at a pressure of 300 pounds per square inch. In both cases the test strips were died out prior to aging.

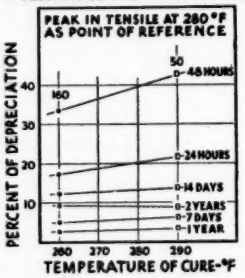
The natural aging was that known as shelf aging, at room temperature in the dark, with test slabs separated by sheets of porous cardboard. The test strips were not cut until after the aging period was ended.

Discussion of Results

Initial Physical Properties. In Figures 1, 2, and 3 are plotted the initial modulus (stress at 400 per cent elongation) and tensile values for the two stocks. Two series of tests on stock II were made. The first of these will be referred to as II A (Figure 2), and the second as II B (Figure 3).

The effect of curing temperature on the original tensile properties in the case of stock I is clearly illustrated in Figure 1. There is no appreciable difference in maximum tensile strength over the entire range of temperatures from 280° F.

FIG. 9 - PERCENTAGE CHANGE IN TENSILE STRENGTH ON AGING vs. TEMPERATURE OF CURE - STOCK II B



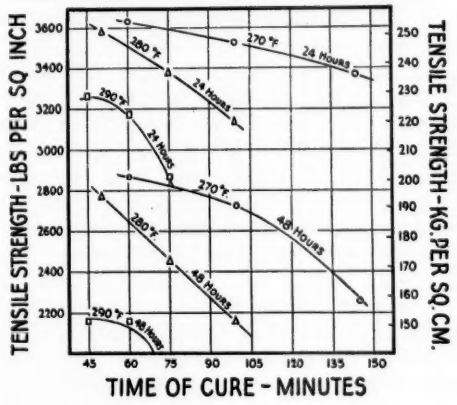
(138° C.) to 320° F. (160° C.), with the exception of that at 280° F. Why this figure was low is not known.

The values for tensile strength of stock II A (Figure 2), which was cured at 270°, 280°, and 290° F. (132°, 138°, and 143° C.), might be considered as equal. However the direction is uniformly toward higher figures with decreasing temperature. The same is also true of stock II B, which was cured at 260° and 290° F., or 127° and 143° C. (Figure 3). Although the differences are not great, and might even be considered within experimental error, the direction appears sufficiently definite to be considered of significance. The fact that stock I showed no better properties with decreasing curing temperature, while stock II gave indications of improvement, might be attributed to the fact that two very different types of accelerators were used.

Geer Oven Aging. The tensile values for stock I, after aging for 8 days in the Geer oven, are plotted in Figure 4. As the method of choosing the proper cures for comparison is a question concerning which there has been considerable

argument, three different points of reference have been chosen. These are the "peaks" in the original modulus, original tensile, and natural aging curves. For simplicity the results are presented in Figure 5, in which the percentage depreciation in tensile strength after aging is plotted against curing temperature. The period of cure is indicated above each point on the curves. The curves are not smooth in either case, but both lead to the same conclusion—namely, that there is definite evidence of greater depreciation or poorer aging when higher curing temperatures are used.

FIG. 10 - TENSILE STRENGTH AFTER ACCELERATED AGING - STOCK IIB - OXYGEN BOMB



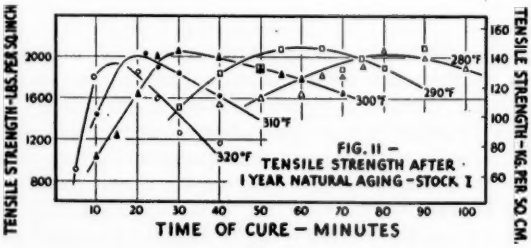
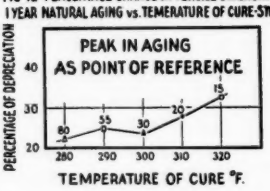


FIG. 11 - TENSILE STRENGTH AFTER 1 YEAR NATURAL AGING - STOCK I

The tensile values for stock II A, after oven aging for 7 and 14 days, are plotted in Figure 6. The percentage depreciation in tensile strength at the end of these aging periods has also been plotted (Figure 7). In this case the initial physical properties do not give sufficient information per se for choosing comparable cures at the different temperatures (Figure 2). The curing range of this stock is so broad that the peaks in neither the modulus nor tensile curves are sufficiently well defined for use as reference points. This being the case, it was decided to use, as the point of reference, the 75-minute cure at 280° F. (138° C.), which is known by long experience with

stock II to be a good technical cure. It will be noted that this cure has the highest tensile strength in the 280° F. range of cures, and also that its modulus is nearly maximum. The cures at 270° F. (132° C.) and at 290° F. (143° C.), which are compared with this 75-minute cure, were selected by calculation from the temperature coefficient for mercaptobenzothiazole stocks established by Park (*12*). These are 110 minutes at 270° F. (132° C.) and 50 minutes at 290° F. (143° C.). From Figure 7 it is clear that any differences in depreciation due to curing temperature are small, the trend being favorable to low-temperature curing.

FIG 12-PERCENTAGE CHANGE IN TENSILE STRENGTH ON 1 YEAR NATURAL AGING vs. TEMERATURE OF CURE: STOCK I



In the comparison involving stock II B, the tensile curves after aging are plotted in Figure 8, and the percentage depreciation in tensile strength in Figure 9. The two cures compared are 160 minutes at 260° F. (127° C.) and 50 minutes at 290° F. (143° C.). In both the 7- and 14-day periods of aging, the stock cured at the higher temperature suffered the greater depreciation, though the amount was so small that it might be considered within experimental error.

Oxygen-Bomb Aging. This aging test was conducted only on the stocks (II A and II B) that were accelerated with mercaptobenzothiazole. The tensile figures after the aging periods (24 and 48 hours) are shown in Figures 10 and 8. The curves (Figures 7 and 9) show appreciably greater percentage depreciation in the samples cured at the higher temperature.

Natural Aging. The 1-year natural aging data on stock I are plotted in Figure 11, and the percentage depreciation figures in Figures 5 and 12. Inspection of the percentage depreciation curves of Figure 5 shows unmistakably better aging at the lowest temperature of cure, with the depreciation increasing quite regularly with increasing curing temperature. This trend is the same in the percentage deterioration curve plotted in Figure 12, where the peaks in the tensile curve (Figure 11) of the naturally aged samples are used as the points of reference. That the differences are real and not dependent on the choice of best cures is shown by the fact that all three comparisons gave the same result.

In the case of stock II A, data on two periods of natural aging are available (1 and 2 years). The tensile figures are plotted in Figure 13, with the percentage depreciation in Figure 7. The curves for both periods show only a trend toward better aging at lower temperatures. In the case of stock II B (Figures 14 and 9), the percentage depreciation in tensile strength appears to be quite independent of whether the stock was cured at 260° F. (127° C.) or 290° F. (143° C.)

The writers feel that the trend in aging in stock II—both

A and B—is sufficiently definite to warrant the conclusion that there is value in low-temperature curing, even in the presence of an antioxidant and an accelerator with a broad curing range such as mercaptobenzothiazole. With such a stock, natural aging data extending only through a period of 2 years cannot be expected to show large differences. Fortunately, sufficient portions of the test slabs remain for the continuation of aging for two additional periods. The writers hope to publish the data on these when they are available.

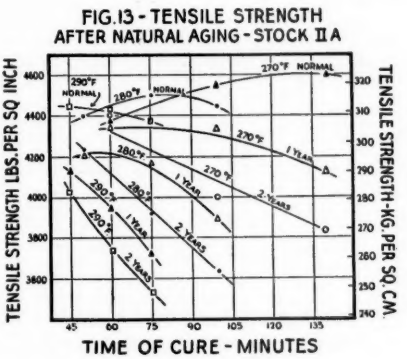


FIG. 13 - TENSILE STRENGTH AFTER NATURAL AGING - STOCK II A

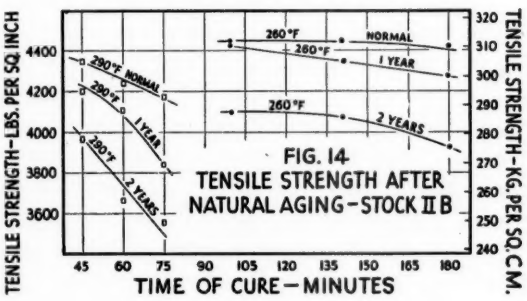


FIG. 14
TENSILE STRENGTH AFTER NATURAL AGING - STOCK II B

Acknowledgment

The writers are indebted to H. F. Palmer and L. V. Cooper for some of the data presented in this report, and to Miss Hilda Albaugh for collecting the literature and assisting in the editing. Appreciation is also due to N. Johnston and O. L. Riley for drawing the curves.

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Grit in Carbon Black

Effect on Flexing Resistance of Vulcanized Rubber

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Rubber channel black has been found to contain amounts of grit retainable on a 325-mesh screen varying from 0.05 to 1.7 per cent. This residue is shown to be objectionable from the standpoint of the flexing resistance of the resulting rubber compounds, higher concentrations being correspondingly more harmful than lower concentrations. The coarser fractions appear to give rise to larger cracks and earlier appearance of cracking than the finer material. Even that which passes a 200-mesh screen but is retained on a 325-mesh is objectionable.

THAT the grit found in carbon black used in rubber products is detrimental to the quality of such products has been pointed out by a number of investigators. Gallie (*5*) states that the presence of this impurity in gas black used for rubber manufacture may be expected to give rise to trouble in the following directions, among others: (1) degradation of tensile and other mechanical properties; (2) production of discontinuity in rubber films required to retain or exclude gases or liquids; (3) unsatisfactory surface finish on goods prepared by extruding, calendering, and spreading; and (4) points of weakness in rubber articles subjected to severe mechanical usage or repeated compression and stressing. Gallie records the finding that the addition of 5 per cent of grit, collected on an 80-mesh screen, to a rubber-sulfur mix (95:5) resulted in reducing the tensile strength

from 1.0 kg. per sq. mm. to 0.75 kg. per sq. mm. Reduction of the grit to finer particle size by grinding caused it to function "merely as a filler." Kearsley and Park (*7*) concur in this opinion. In their work the grit was ground to pass a 100-mesh screen, and was then added to the standard black sample, in amounts varying from 0 to 10 per cent. The results indicated that in amounts up to 3 per cent this material had no measurable effect on the tensile strength or modulus of the stock.

Twiss (*9*) concluded that grit has no effect on abrasion resistance although it may lower tensile strength. His procedure was as follows: Mixing A contained no grit (90 mesh), B contained a different black having 0.09 per cent grit, and C contained the same black as A, except that enough of the grit separated from another sample of the black used in B was added to give a sample containing 0.1 per cent. Tests on these samples showed the tensile strengths to be 2.03, 1.84, and 1.92 kg. per sq. mm., respectively. Abrasion tests showed the abrasion resistance to be 1.03, 1.06, and 1.00, respectively. Thus the variations in abrasion resistance were within experimental error, although lower tensile strengths and resilient energies resulted in the cases of the blacks containing grit.

The difficulties in sampling and in methods of testing carbon blacks for grit are discussed by Murphy (*8*), Gallie and Porritt (*6*), Esch (*3*), and Evers (*4*). These writers have not discussed, however, the effect of grit on the quality of the resulting rubber product.

The evidence points to the conclusion that the coarser grit lowers tensile strength, the fine grit is not detrimental to tensile strength, and that neither is objectionable from the standpoint of abrasion resistance. Experimental data on its effect on flexing resistance, which is of distinct importance in the compounding of tire treads and sidewalls, where the major amount of rubber channel black is used, do not appear to have been recorded in the literature.

The flexing resistance of rubber compounds is becoming of increasing importance. In the past, the major cause of tire failures under normal operating conditions has been tread wear. The increase in power and in braking facilities on the newer cars is causing still faster wear. To overcome this difficulty, the rubber compounder is naturally turning to the use of higher black loadings to make the tires more resistant to abrasion. The increased loading in itself, through the increase in volume of pigment and through the stiffening of the compound, will lead to a greater tendency toward flex-cracking. Even under present conditions, tires occasionally crack. This leads to an unsightly appearance and raises the question in the mind of the user as to the length of service that will be rendered. Consequently it appears timely to present data on the effect of carbon black grit on the flexing resistance of rubber.

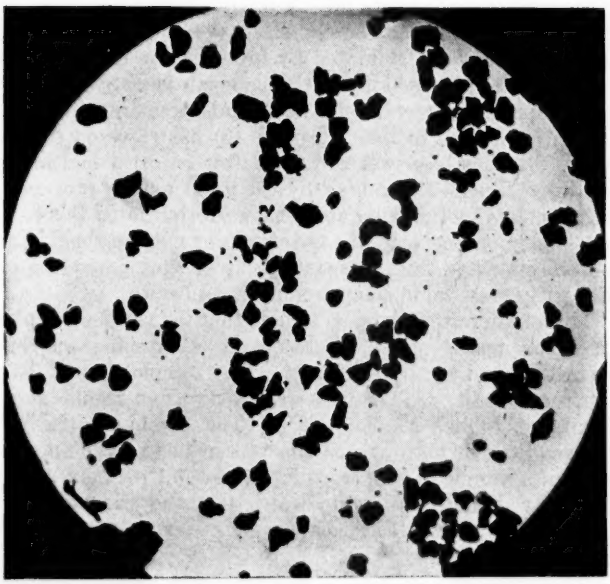
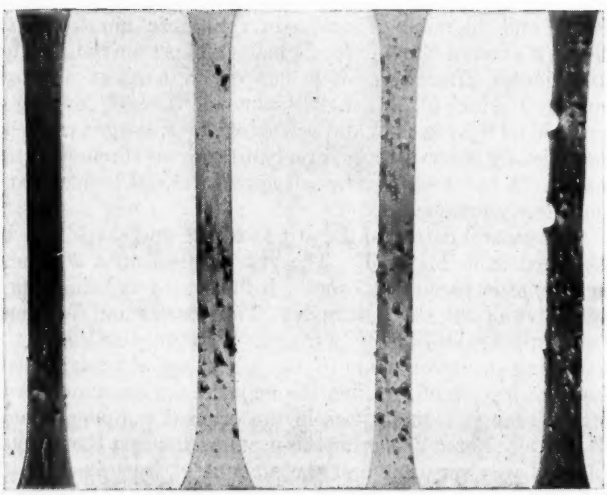


FIGURE 1. CARBON BLACK GRIT



A B C D

FIGURE 2. EFFECT OF TOTAL RESIDUE ON 325-MESH SCREEN
Grit added to tread masterbatch

Testing Procedure

The grit used in this work was separated from the black by wet-screening on a 325-mesh sieve (44-micron openings). The operation was facilitated by brushing the black on the screen to assist in breaking up the aggregates and by directing a fine spray of water (under 20 pounds pressure) onto the screen from time to time. Endres (*2*) has reported that a black that has been wet can thereafter be dried and satisfactorily dispersed in rubber by the usual milling processes. Experiments in this laboratory have substantiated this conclusion. Consequently, the wet-screening method should not be objectionable from the standpoint of subsequent use of the gritty material in compounding experiments.

It is of interest, in passing, to note that the various samples of black tested showed percentages of residue varying from 0.05 to over 1.00 per cent. One sample showed 1.74 per cent of grit. All samples were taken from regular shipments of rubber channel black. The combined residues showed little or no tinctorial effect as judged by the appearance of a sample of pale crepe into which 0.1 per cent of the residue was milled. This indicated that the grit contained little or no aggregated black—i. e., soft aggregates which would disperse easily.

This method has proved of considerable interest and value in examining residues from screening tests and their dispersability in rubber. A sample of pale crepe amounting to approximately 500 grams is broken down in the usual manner, allowing 4 to 5 minutes for breakdown. The residue is then added and the milling continued for 10 more minutes. The batch is allowed to stand for 24 hours and is then remilled for 10 minutes, after which it is cut off in a sheet approximately 0.05 inch (0.127 cm.) in thickness. A batch containing grit will be light in color and still translucent, the grit particles being easily observable and evenly distributed throughout the batch. A batch containing soft aggregates will be black and completely opaque.

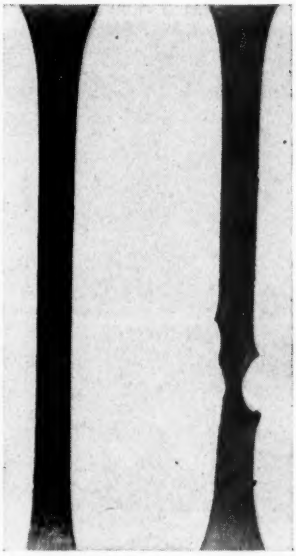
The general nature of the grit as to size and shape may be obtained from Figure 1. The grit retained on a 200-mesh screen, after passing 100 mesh, is illustrated as being representative of the other samples. The coarser and finer material appeared to differ only in size. It is probable that in the screening operation some, if not all, of the sharper corners have been worn off, making the material appear more nearly round than it actually was in the original sample of black. It was also noted in making this examination that the amount of sand was very low and the amount of iron oxide, with adhering black, represented a relatively small percentage of the total.

In testing the effect of grit on flexing, a masterbatch of tread stock, containing an easily dispersible black of low grit content (0.10 per cent), was used. Varying amounts of grit were milled into portions of this batch. All batches, including the control,

were remilled after standing for 24 hours. In this way the grit received two millings, giving it every opportunity for satisfactory dispersion. The formula of the masterbatch was as follows:

Smoked sheets	100
Sulfur	2.75
Zinc oxide	6
Pine tar	3
Stearic acid	3.5
Carbon black	46
Mercaptobenzothiazole	0.75
	162.00

Test slabs were cured for 60 minutes at 280° F. (137.8° C.) which was judged to be the optimum commercial cure.



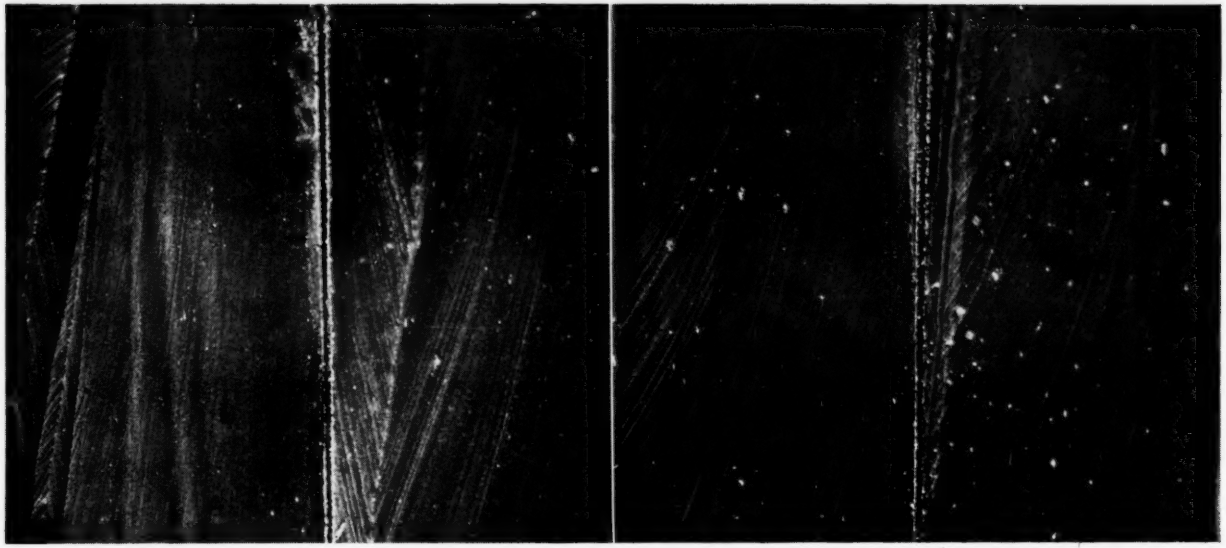
A E

FIGURE 3. EFFECT OF GRIT ADDED TO BLACK BEFORE MILLING

Dumbbell test strips were died out in the usual manner. The flexing tests were carried out on the Firestone flexing machine (*1*), the test strips being flexed to 100 per cent elongation at the rate of 400 flexes per minute. Experience over the past six years has shown that this test parallels drum and road tests unusually well.

FLEXING TESTS

The flexing results on stocks containing varying amounts of the total residue on a 325-mesh screen are shown in Figure 2. The control stock is marked A. The amounts of grit added were 0.5 per cent (B), 1.0 per cent (C), and 2.0 per cent (D).

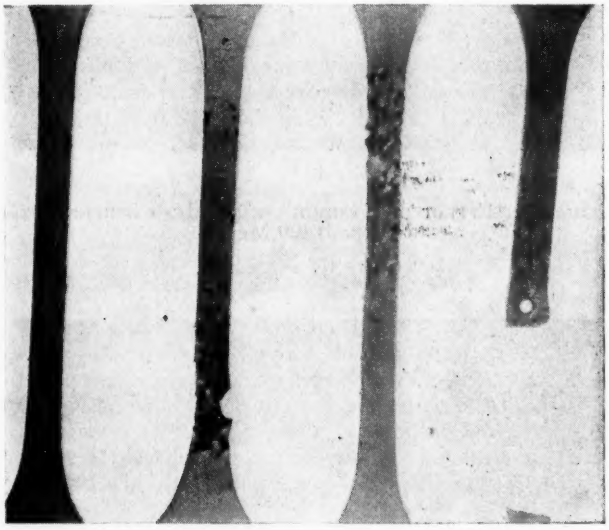


A B C D

FIGURE 4. APPEARANCE OF STOCKS CONTAINING GRIT

The concentrations of grit are given as percentages of the total black content of the stock. The strips with the high grit content (C and D) were removed from the flexing machine after 3.5 hours, as the cracking was severe at the end of that time. The remaining two strips were flexed 4.5 hours. As the test does not lend itself to numerical evaluation, the comparison is made by visual observation of the test strips after a given time of flexing, judging by the number and intensity of the cracks. The photograph shows that the stock containing 0.5 per cent of added grit (B) has cracked more than the control, and that those with higher percentages (C and D) are correspondingly worse. This and subsequent tests have been duplicated.

In order to determine whether the method of mixing

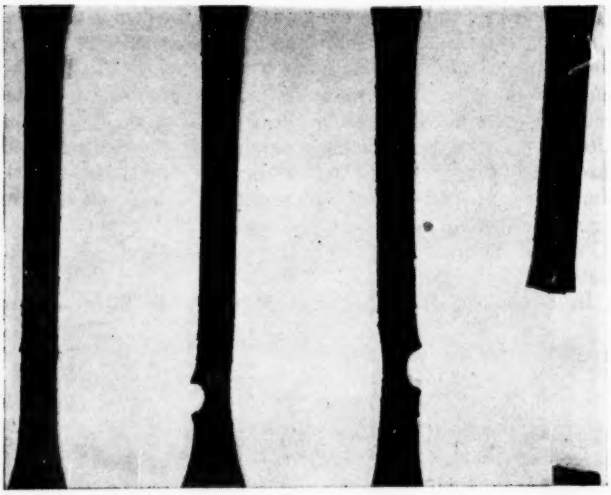


A F G H

FIGURE 5. EFFECT OF RESIDUE ON 100-MESH SCREEN AFTER PASSING 40 MESH

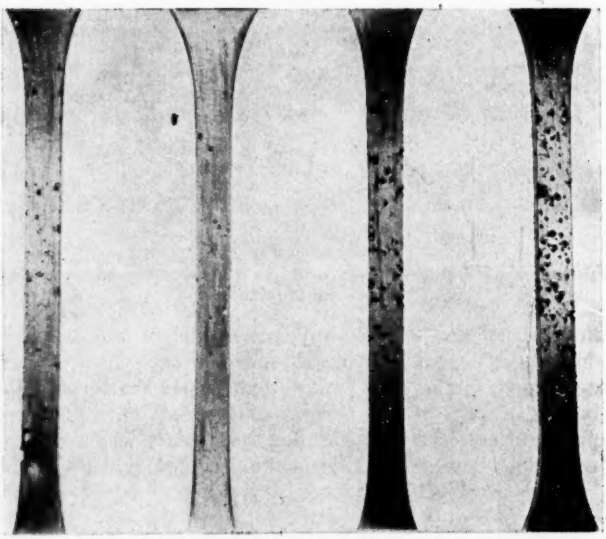
affected the results materially, a comparison was made in which 1.0 per cent of grit was added directly to the black itself before mixing (E), rather than to the masterbatch as above. Results of this test are shown in Figure 3. It is apparent that the strip containing the black to which grit has been added has cracked decidedly more than the control. Comparison of the two stocks containing 1.0 per cent of added grit—E in Figure 3, and C in Figure 2—shows that the method of adding the grit makes no appreciable difference in the results.

For the purpose of obtaining additional evidence as to whether the grit was uniformly dispersed in the batch, the test slabs were examined microscopically. A typical case is



A I J K

FIGURE 6. EFFECT OF RESIDUE ON 200-MESH SCREEN AFTER PASSING 100 MESH



A A L L

FIGURE 7. EFFECT OF RESIDUE ON 325-MESH SCREEN AFTER PASSING 200 MESH

illustrated in Figure 4. In order to obtain a field sufficiently large to be representative of the entire surface, very low magnification was used. A grit particle at or near the cut surface of the sample causes a "hump" or unevenness. These are readily observable using reflected light. Thus, in Figure 4 it is noted that the number of such humps becomes increasingly greater in comparing the stocks in the order A, B, C, and D. In all stocks these were uniformly distributed over the field, showing uniform distribution of the grit. The high magnifications normally used in examining treads, with the methods now employed, are not applicable to stocks containing grit. The grit retained on a 325-mesh screen must be approximately 44 microns in one direction, whereas the thickness of a slide from a tread must be less than one-tenth of this thickness in order to be examined by transmitted light.

It then appeared desirable to determine how coarse the grit must be to affect flexing adversely. A 10-gram portion of the 325-mesh residue was screened successively through 40-, 100-, 200-, and 325 mesh sieves. It is of interest to note the relative amounts collected on the various screens:

On	Through	Amt. %
40 mesh	....	4.4
100 mesh	40 mesh	24.0
200 mesh	100 mesh	47.2
325 mesh	200 mesh	24.2

The fact that the percentage remaining on the 325-mesh sieve after passing the 200 mesh is smaller than that collected on the 200-mesh screen, is again indicative that it is grit or foreign material rather than agglomerated black. Were this material agglomerated black, normal distribution of the range of particle size would require increasing amounts of residues with decreasing size of mesh openings of the various screens.

The flexing results shown in Figure 5 are those obtained in the comparison of the control, A, with stocks to which had been added 0.5 per cent (F), 1.0 per cent (G), and 1.5 per cent (H) of the material passing 40 mesh, but remaining on a 100-mesh sieve. It was again observed that stock F, to which 0.5 per cent had been added, cracked more than the control A. The higher grit loadings appeared worse.

In the same way, Figure 6 shows the test strips containing 0.5 per cent (I), 1.0 per cent (J), and 1.5 per cent (K) of the residue passing 100 mesh, but remaining on a 200-mesh sieve. Again, 0.5 per cent was found to have affected the flexing adversely, with higher concentrations showing still greater differences.

One concentration only was used in testing the residue on a 325-mesh screen that had passed 200 mesh. The results are recorded in Figure 7. In this case two strips each of the control A and the similar stock to which 0.5 per cent of the

grit was added, L, are shown. Again it appeared that 0.5 per cent was harmful.

TABLE I. VALUES FOR TENSILE STRENGTH

STOCK	ADDED GRIT %	TENSILE STRENGTH *Lb./sq. in.*
TOTAL RESIDUE ON 325 MESH		
A	0.0	4125
B	0.5	4025
C	1.0	3975
D	2.0	3950
RESIDUE PASSING 40, REMAINING ON 100 MESH		
A	0.0	4075
F	0.5	3975
G	1.0	4000
H	1.5	3975
RESIDUE PASSING 100, REMAINING ON 200 MESH		
A	0.0	4075
I	0.5	4225
J	1.0	4075
K	1.5	4075
RESIDUE PASSING 200, REMAINING ON 325 MESH		
A	0.0	4000
L	0.5	4075

EFFECT OF GRIT ON TENSILE STRENGTH

In view of the previously reported findings as to the effect of grit on tensile strength, it is of interest to note the values for tensile strength obtained in these tests. Strips from the same slabs were used in the tensile and flexing comparison. These values are given in Table I. Four strips were broken and averaged in arriving at the recorded values. All slabs were cured 60 minutes at 280° F. (137.8° C.).

All tensile-strength values are probably within the limits of experimental error. In these tests, the stocks containing the coarser grit show indications of a very slight lowering of tensile strength (stocks B, C, D, F, G, and H compared to stock A). However, the general conclusion is reached that the fine grit does not lower tensile strength in the concentrations used in these tests. It has been noted, in tests not reported, that in many cases the presence of relatively high percentages of grit leads to more erratic "breaks" than are normally encountered in testing treads containing blacks of low grit content.

No attempt has been made to draw a comparison of the relative effects of the different sizes of grit. The indications are, however, that the coarser material leads to larger cracks and to earlier cracking, whereas the finer material gives rise to a large number of small cracks. In this respect, the results are similar to those produced by any ground pigment.

ACKNOWLEDGMENT

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